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## BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

## Division of Chemical Science

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## CONTENTS

	PAGE	RUSS. PAGE
Program for the Building Up of Communism .....	1611	1725
INORGANIC AND ANALYTICAL CHEMISTRY		
Reactions in the Solid Phase of Silica with Oxides of Rare Earth Elements ( $\text{La}_2\text{O}_3$ , $\text{Nd}_2\text{O}_3$ , $\text{Gd}_2\text{O}_3$ ). É. K. Keler, N. A. Godina, and E. P. Savchenko.....	1613	1728
Reactions in the Solid Phase between Silica and Praeseodymium Oxide. É. K. Keler, N. A. Godina, and E. P. Savchenko .....	1619	1735
PHYSICAL CHEMISTRY		
An Investigation of the Structure and Reactivity of Some Stable Radicals. M. B. Neiman and A. L. Buchachenko.....	1624	1742
Polarographic Study of the Effect of Temperature on the Protonation Rate of the Maleic Acid Di-anion. S. G. Mairanovskii and L. I. Lishcheta.....	1631	1749
The Inductive Effect in the Oscillational Frequencies of the Bonds Ge-H and Ge-D. V. A. Ponomarenko, G. Ya. Zueva, and N. S. Andreev .....	1639	1758
The Effect of the Thermodynamic Isotope Effect on the Distribution of Isotopic Molecules. G. A. Skorobogatov.....	1644	1763
ORGANIC AND BIOLOGICAL CHEMISTRY		
Tautomerism and Geometric Isomerism of Nitrogen-Containing Derivatives of Carbonyl Compounds. Communication 5. Polarographic Study of Semicarbazones and Thiosemicarbazones of Aromatic Aldehydes. Yu. P. Kitaev, G. K. Budnikov, and A. E. Arbuzov.....	1652	1772
Preparation of (Ethylcyclopentadienyl)manganese Tricarbonyl. A. N. Nesmeyanov, K. N. Anisimov, and Z. P. Valueva.....	1659	1780
Synthesis and Study of the Reactivity of Polymerizable Organometallic Derivatives of p-Vinylbenzoic Acid. M. M. Koton and T. M. Kiseleva.....	1662	1783
Telomerization of Dimethylcyclsiloxanes. Communication 3. Telomerization Reactions with Dichloromethylvinylsilane and Dichloromethylphenylsilane. K. A. Andrianov and V. V. Severnyi.....	1666	1788
Reaction of Trialkyl (or Aryl) Silanols with (Ethoxymethylsilyl)methyl Dimethylphosphinates. K. A. Andrianov and I. K. Kuznetsova .....	1670	1792
Rearrangement Occurring in the Dehydrochlorination of 1,1- and 1,2-Bistrichlorosilyl-1,2- dichloroethanes with Aluminum Chloride. V. F. Mironov and V. V. Nepomnina.....	1673	1795
Synthesis of Surface-Active Substances from $\omega$ -Chloro Carboxylic Acids. S. A. Dmitriev, N. M. Karavaev, and A. V. Smirnova.....	1678	1800
Synthesis of 4,6,7,8-Tetrahydro-5-vinyl-2(3H)-naphthalenone and Its Condensation with 2-Methyl-1,3-cyclohexanedione to Give 14 $\xi$ -Hydroxy-D-homo-19-norandrost- 4,9(10)-diene-3,17a-dione. N. N. Gaidamovich and I. V. Torgov .....	1682	1803

# CONTENTS (continued)

	PAGE	RUSS. PAGE
Heterogeneity of Nitrolignin. A. A. Chuksanova, O. P. Grushnikov, and N. N. Shorygina.....	1688	1810
Raman-Spectrum Investigation of the Conformations of the Cyanohydrins of Some Cyclohexanone Derivatives. M. I. Batuev, A. A. Akhrem, A. V. Kamernitskii, and A. D. Matveeva.....	1691	1813
Stereochemistry of Heterocyclic Compounds. Communication 7. Steric Structures of Octahydro-4(1H)-quinolone Derivatives and the Configurations of Decahydro-quinolines. É. A. Mistryukov and V. F. Kucherov.....	1695	1816
Stereochemistry of Heterocyclic Compounds. Communication 8. Debenzoylation and Stereochemistry of Decahydroquinoline and Its Derivatives. É. A. Mistryukov and V. F. Kucherov.....	1702	1826
Chemistry of Acetals. Communication 8. Grignard Reactions with 1,1,3,3-Tetraethoxypropane, 1,1,3,5,7,7-Hexaethoxyheptane, and 1,1,3,5,7,9,9-Heptaethoxynonane. L. A. Yanovskaya and V. F. Kucherov.....	1706	1830
Pyridine Bases Derived from 1-Buten-3-yne. Communication 7. Synthesis of Pyridine Bases by the Condensation of 2-Methyl-1-buten-3-yne with Ketones and Ammonia. I. L. Kotlyarevskii and E. D. Vasil'eva.....	1710	1834
Butadiyne Derivatives. Communication 9. Synthesis of Unsaturated Alkoxy and Alkylthio Acetals Having C <sub>7</sub> -C <sub>15</sub> Carbon Chains in Their Molecules. A. V. Bogdanova, G. I. Plotnikova, and I. P. Yakovlev.....	1715	1841
Alkylation of Phenols with Compounds with Mixed Functions. Communication 3. Alkenylation of m- and p-Cresols with 3-Buten-1-ol. N. I. Shuikin, E. A. Viktorova, I. E. Pokrovskaya, and T. G. Malysheva.....	1720	1847
Alkylation of Phenols with Compounds with Mixed Functions. Communication 4. Alkenylation of m- and p-Cresols with 4-Penten-1-ol. N. I. Shuikin, E. A. Viktorova, I. E. Pokrovskaya, and T. G. Malysheva.....	1725	1851
Catalytic Synthesis of Nitriles. Communication 5. Conversion of Isoalkanols into Nitriles by Means of Ammonia. M. A. Popov and N. I. Shuikin.....	1729	1855
Determination of the Individual Hydrocarbon Composition of Tartary Petroleum. Communication 6. Ligroin from Petroleum from the Shugurov Deposits. B. Le, F. A. Urmancheev, I. P. Lipatova, R. G. Bukharaeva, and I. A. Lamanova.....	1732	1858
Composition of the Butenes Formed in the Catalytic Dehydration of 2-Butanol. A. A. Balandin, E. I. Klabunovskii, and E. F. Litvin.....	1737	1863
Catalytic Hydrocondensation of Carbon Monoxide with Olefins and Their Hydropolymerization Under the Action of Carbon Monoxide and Hydrogen. Communication 33. Formation of Higher Hydrocarbons with a Nonmultiple Number of Carbon Atoms with Respect to the Original Olefin. N. I. Ershov, Ya. T. Éidus, and V. R. Erokhina.....	1744	1871
Catalytic Hydrocondensation of Carbon Monoxide with Olefins and Their Hydropolymerization Under the Action of Carbon Monoxide and Hydrogen. Communication 34. Mutual Transitions of the Reactions of the Formation of Hydrocarbons from Mixtures of Ethylene, Hydrogen, and Carbon Monoxide. Ya. T. Éidus, N. I. Ershov, and V. R. Erokhina.....	1747	1874
Composition of Products of the Bromination of 2-Thienyl Ketones in Presence of Excess of Aluminum Chloride. Yu. B. Vol'kenshtein, B. V. Lopatin, and V. A. Petukhov.....	1752	1879
<b>BRIEF COMMUNICATIONS</b>		
An Improved Method of Determining Surface Area by the Absorption of Air. A. L. Klyachko-Gurvich.....	1756	1884

# CONTENTS (continued)

	PAGE	RUSS. PAGE
The Synthesis of Alkenylsilanes by the High-Temperature Condensation of Unsaturated Compounds with Silicon Hydrides. V. F. Mironov and V. V. Nepomnina ..	1759	1886
The $\beta$ -Alloxymethyl n-Butyl Acetal of Acetaldehyde. A. K. Gorban' .....	1761	1889
The Reaction of Poly-(vinyl Alcohol) with Poly-(methacrylic Acid). M. F. Shostakovskii, A. M. Khomutov, and N. M. Khomutova ...	1763	1890
Phase Transformations in the Preparation of Ni-MgO Catalysts by the Decomposition of Oxalates in a Current of Hydrogen. V. M. Akimov, E. F. Litvin, A. M. Rubinshtein, and L. Kh. Freidlin .....	1765	1892
The Production of Dialkylaluminum Hydrides from Dialkylaluminum Halides and Sodium Hydride. L. I. Zakharkin and I. M. Khorlina .....	1768	1894
The Dichlorides of p-Styrylphosphonous and p-Styrylphosphonic Acids. M. I. Kabachnik and E. N. Tsvetkov .....	1770	1896
The Decomposition of Phenylidiazonium Borofluoride in Nitrobenzene in the Presence of Zinc, Cadmium, and Silver Powders. L. G. Makarova and M. K. Matveeva.	1772	1898
The Oxidation of Low-Molecular-Weight Hydroxyl Compounds with Oxides of Nitrogen. N. Ya. Lenshina, M. F. Denikeeva, and V. I. Ivanov .....	1774	1899
1-Cyclopropyl-2- $\alpha$ -furylcyclopropane and Its Conversions. A. P. Meshcheryakov, V. G. Glukhovtsev, and N. N. Lemin .....	1776	1901
The Magnetic Susceptibility of Derivatives of Salicylalimine and Some Other Organic Compounds. V. I. Belova and Ya. K. Syrkin .....	1778	1903
Oxidative Polycondensation of Diacetylenes. I. L. Kotlyarevskii, L. B. Fisher, and E. S. Domnina .....	1780	1905
Synthesis of Diquaternary Ammonium Salts of Hexamethylenediamine. M. F. Shostakovskii, V. P. Denisenko, and A. K. Gorban' .....	1782	1907
Synthesis of 1,10-Decanedicarboxylic Acid from Cyclododecatene-1,5,9. L. I. Zakharkin, V. V. Korneva, and G. M. Kunitskaya .....	1784	1908
Fluorinated Monocarboxylic Acids. I. L. Knunyants, Li Chai-Yuan, and V. V. Shokina .....	1785	1910
Use of the Reaction between Dilithioorganic Compounds and Metal Halides to Synthesize Polymers with a Conjugated System of Double Bonds. V. Ya. Bogomol'nyi and B. A. Dolgoplosk .....	1787	1912
Structure of the Complex Compounds of Diphenylboron Chloride with Primary Amines. B. M. Mikhailov and N. S. Fedotov .....	1788	1913
Synthesis of DL-19-Nor-d-homotestosterone and Its 17 $\alpha$ -Alkylhomologs. S. N. Ananchenko, V. M. Rzhaznikov, V. N. Leonov, and I. V. Torgov .....	1789	1913
General Meeting of the Division of Chemical Science of the Academy of Sciences, USSR. .	1790	1915



## PROGRAM FOR THE BUILDING UP OF COMMUNISM

Translated from *Investiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,  
No. 10, pp. 1725-1727, October, 1961

The new draft Program of the Communist Party of the Soviet Union, now known throughout the whole world, may be fairly assessed as the most important political document of our time. The program is divided into stages of development of the struggle to build up communism, to achieve the century's ambition of the whole people. The project gives expression to all the wealth of ideas and principles of communism; it is the magnificent plan of the activity of the Soviet people, of our party, of our country. A characteristic feature of the program is its amazing range combined with the absolute realism of all its items.

The draft Program contains a short scientifically based statement of the tasks and aims of the party in the period of development of the structure of communism and lays down its basic strategy and tactics. This document, based on the fundamental principles of Marxist-Leninist theory and on a profound scientific analysis of contemporary developments, solves in a new way a number of the important theoretical problems of Marxism-Leninism.

In the first pages of the draft Program we read of the high aim of the party - "to construct a communist society whose token is: 'From each according to his powers, to each according to his needs.'" It embodies in full measure the party slogan: "All in the name of the people, all for the good of the people." The introductory chapter finishes with the solemn declaration: "Communism fulfills a historic mission to free all men from social inequality, from all forms of oppression and exploitation, and from the horrors of war, and to establish on the earth Peace, Truth, Freedom, Equality, and the Cooperation of all peoples."

Productive forces and science have achieved enormous development in our time, but, as noted in the Program: "If the twentieth century has not yet seen an end to the poverty of hundreds of millions of people, nor brought material abundance and spiritual welfare to all people on the Earth, this is due only to capitalism."

Now, thanks to the labor of the Soviet people and the many-sided activities of our party, "mankind has achieved a real existing socialist society and is engaged on the scientific experiment of building up socialism. The road to socialism is signposted. Many people are travelling along it, and all peoples will travel it sooner or later."

It should be noted that bourgeois ideology in the U.S.A. and other capitalist countries endeavours to show "scientifically" that "socialism" or "the welfare state" can also be created under capitalism, but the sad reality refutes these idle claims, and bourgeois theories of "planned" capitalism "without crises" are buried in the dust by the whole course of development of contemporary capitalist economy.

Increase in production in the capitalist world is depressed by the conflict between governments, whereas the development of each separate socialist country leads to a general increase and strengthening of the forces of socialism. "The cooperation of socialist countries", called for in the Program, "enables each to make full use of its resources in the most rational way for the development of its productive forces. In the process of the economic and scientific and technical collaboration of socialist countries, the coordination of national economic plans, specialization, and cooperation in production lead to a new type of international division of work." In recent years there has been a great increase in international contacts between Soviet scientists, and a greater development in scientific and technical cooperation between the countries of the socialist camp, particularly with respect to a number of basic problems in the field of chemistry.

Our party and our people have set as their main economic task to create, in the course of two ten year periods, the material and technical basis for communism, and will provide complete electrification of the country and improve techniques and technology in industry and rural economy. There will be a wider use of chemistry in the national economy and great developments associated with progress in the chemistry of new branches of industry, particularly in the field of various synthetic products and materials and of metallic alloys with new properties. The organic combination of science and production leads to a rapid tempo of scientific and technical progress. "The development of new techniques", called for in the Program, "will be used for radical improvements in the working conditions of the



Soviet people, reduction in the working day, well organized living conditions, liquidation of heavy physical work and later of all unskilled work."

It is stated in the draft program that the Communist Party of the Soviet Union intends to increase the volume of industrial production during the next ten years by a factor of about two and a half, thus exceeding the present level of production in the U.S.A., and to increase it over 20 years by a factor of no less than six, leaving far behind the total volume of production in the U.S.A.

One of the most important tasks of national economy will be to increase the production of metals and fuels and every sort of development in chemical industry. The draft program states: "There will be a special increase in the production of light, nonferrous, and rare metals, with particular emphasis on increased aluminum output... This will successively follow the line of essential supplies of oil and gas, which will also be used increasingly as raw materials for chemical industry." The development of chemistry and the full use of its achievements will ensure the introduction of more up-to-date and economical means of production and products to suit national requirements. Metals and wood will be utilized more economically in building construction, together with light synthetic materials. There will be a rapid growth in the output of chemical fertilizers and various agents for protecting agriculturally valuable plants.

The Program lays down that: "The Party will support in every way the further strengthening of the role of science in the construction of communist society... the widespread and rapid introduction of new scientific and technical achievements into practice." Particularly important for the development of chemistry is "a resolute increase in experimental work, including that immediately directed to production." Continuous modernization of technology will be accompanied, in a number of processes, by the use of chemical instead of mechanical treatment of materials. Electrochemistry, semiconductor instruments, and radioelectronics will have an important part in technological processes.

The Party believes that an important task in the scientific field is the development of theoretical investigations in mathematics, physics, chemistry, and biology; these are essential to the development and effectiveness of various technical, medical, agricultural, and other sciences. Chemistry has the enormous tasks of investigating means for the best utilization of our natural resources in energy, of discovering a means for the direct conversion of chemical into electrical energy, and of developing theoretical bases for new technological methods, in particular methods for creating artificial and synthetic materials for all branches of the national economy. There should be extensive developments in the search to create new chemical products for use in medicine and agriculture.

The draft Program speaks of "a guarantee of the fruitful development of science, firmly linked with the constructive work of the people, the practice of communist construction..."

It is emphasized in the Program that scientific institutes should plan and coordinate their work along the most important directions for research, corresponding to the plans for development of national economy and culture. Of great importance for the development of Soviet science are the activities of the State Committee of the Soviet of Ministers of the USSR for the Coordination of Scientific Research Work. Leading chemical scientists have already participated in its work, and head a number of the scientific soviets created by the Committee. They have already coordinated plans for chemical investigations, of value to the whole country, which depend for their fulfillment on the resources of academic institutes, colleges, and the scientific institutes of the State Committee of Ministers of the USSR for Chemistry. It remains for Soviet scientists and the boards of the Presidium of the Academy of Sciences of the USSR and the Division of Chemical Sciences to draw up a clear statement of the proposed plan for the next few years, with respect to the separate problems.

Soviet chemical scientists have welcomed with profound satisfaction the words of the draft Program of the Communist Party of the Soviet Union: "The Party will take measures for the further strengthening and development of the material basis of science and for the drawing in to scientific activity of the most capable creative forces."

This place of honor for Soviet chemists will shortly give them a leading position in the world of chemistry, and they will play their part in ensuring the leadership by our country in all branches of the scientific world.

The Twenty-Second Session of the Communist Party of the Soviet Union, in confirming the new Party Program, and the collective chemists of the institutes of the Division of Chemical Sciences, in fulfilling the socialist tasks assigned to them for the development of the scientific bases of new technological processes in chemistry and metallurgy and the creation of synthetic materials and products for the industry, medicine, and agriculture of our country, will be building Communism.

## INORGANIC AND ANALYTICAL CHEMISTRY

### REACTIONS IN THE SOLID PHASE OF SILICA WITH OXIDES OF RARE EARTH ELEMENTS ( $\text{La}_2\text{O}_3$ , $\text{Nd}_2\text{O}_3$ , $\text{Gd}_2\text{O}_3$ )

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The silicates of the rare earth elements have been little investigated. Recent literature data on these silicates is mainly restricted to statements as to their existence. Warshaw and Roy [1] studied the  $\text{Ln}_2\text{O}_3$ - $\text{SiO}_2$  system in 1959, and showed that there were two types of compound. The work of Toropov, Bondar', and Galakhov [2-4] in 1959-1961 established the existence of three types of compound in these systems. The authors obtained the silicates from melts. The object of our work was to study the conditions for production of silicates by reactions in the solid phase.

#### EXPERIMENTAL

We selected for investigation the oxide systems:  $\text{La}_2\text{O}_3$ - $\text{SiO}_2$ ,  $\text{Nd}_2\text{O}_3$ - $\text{SiO}_2$ , and  $\text{Gd}_2\text{O}_3$ - $\text{SiO}_2$ . The reaction products were examined by the x-ray method and by chemical and microscopic phase analysis. X-ray analysis was carried out by the powder method, using ionization recording. Chemical phase analysis was based on selective solubility of the unreacted rare earth oxides in a hot solution of ammonium acetate or ammonium nitrate. It should be noted that rare earth silicates were not quite inert to solutions of ammonium salts and dissolved partially on prolonged boiling. This was particularly noticeable for silicates of the composition  $\text{Ln}_2\text{O}_3 \cdot \text{SiO}_2$ . We tested other reagents: alcohol, boric acid, glacial acetic acid, glycine, and trilon B were less effective for selective dissolution, so that we kept to ammonium acetate.

The starting materials were amorphous silica (pure for analysis grade), the oxides  $\text{La}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  containing about 99% of main component, and 98.2%  $\text{Gd}_2\text{O}_3$ . The mixture of oxides was pressed into a tablet and heated in a silit or cryptol furnace.

Interaction of Lanthanum Oxide with Silica. Mixtures of lanthanum oxide and silica, in the proportions 3 : 1, 2 : 1, 1 : 1, 2 : 3, 1 : 2, and 1 : 3, were heated for various times at temperatures from 1100-1650°. The products were analyzed chemically and by x-rays. Table 1 shows the results. It is clear that, after 8 hr at 1200°, part of the lanthanum oxide had already combined with the silica and would no longer dissolve. The amount of silicate formed could be calculated from the difference between the amounts of lanthanum oxide which dissolved from the original material and the fired product. As noted above, lanthanum silicate was also slightly soluble in ammonium acetate, so that the calculated yield of reaction product was slightly low, particularly with a 1 : 1  $\text{La}_2\text{O}_3$  :  $\text{SiO}_2$  mixture. Interaction between lanthanum oxide and silica at 1200° was also shown by the results of x-ray analysis (Fig. 1); these showed the formation of a new phase which was independent of the starting mixture composition over the  $\text{La}_2\text{O}_3$  :  $\text{SiO}_2$  ratio range 1 : 1, 2 : 3, and 1 : 2, since all three products gave the same diffraction patterns. The interplanar separations coincided with the data obtained by Toropov and Bondar' for lanthanum orthosilicate ( $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ ) [2]. According to these authors, the x-ray diffraction patterns of the silicates  $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$  and  $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$  are very similar (the strongest lines of each coincide), so that it was difficult to identify the reaction products by means of only one x-ray analysis. However, careful analysis of a series of x-raygrams enabled us to establish the existence of two phases  $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$  and  $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ , with the orthosilicate as the predominant phase.

It is evident from Table 1 that the amount of soluble lanthanum oxide decreased with increasing firing temperature, indicating that reaction was more complete. At 1600 and 1650°, with material of composition  $1\text{La}_2\text{O}_3 + 2\text{SiO}_2$ , nearly all the lanthanum oxide was converted into silicate. X-ray analysis showed that, up to 1500°, the diffraction patterns were the same for the products from mixtures of different compositions. Only the contents of the original components decreased with increasing ignition temperature. However, new lines, corresponding to the pyrosilicate

TABLE 1. The Phase Composition of Ignited Mixtures of Lanthanum Oxide and Silica

Starting mixture composition				Ignition temp., °C	Heat time, hr.	Lanthanum oxide as percentage of amt. in initial mixture		X-ray analysis data
mole, %		wt. %				Soluble in $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	Combined as silicate	
$\text{La}_2\text{O}_3$	$\text{SiO}_2$	$\text{La}_2\text{O}_3$	$\text{SiO}_2$					
50	50	84,6	15,4	1200	8	70,2	29,8	$\text{La}_2\text{O}_3 + \text{La}_2\text{O}_3 \cdot \text{SiO}_2 + 2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2 + [\text{SiO}_2]^*$
50	50	84,6	15,4	1350	2	58,2	41,8	The same
50	50	84,6	15,4	1500	2	29,9	70,1	$2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{La}_2\text{O}_3 \cdot \text{SiO}_2 + [\text{SiO}_2] + [\text{La}_2\text{O}_3]$
50	50	84,6	15,4	1600	2	27,1	72,9	$\text{La}_2\text{O}_3 \cdot \text{SiO}_2 + 2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2 + [\text{La}_2\text{O}_3]^*$
50	50	84,6	15,4	1650	1,5	26,1	73,5	The same
40	60	78,4	21,6	1200	8	62,1	37,9	$\text{La}_2\text{O}_3 + 2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{La}_2\text{O}_3 \cdot \text{SiO}_2 + [\text{SiO}_2]$
40	60	78,4	21,6	1350	2	47,8	52,2	The same
40	60	78,4	21,6	1500	2	19,0	81,0	$2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{La}_2\text{O}_3 \cdot \text{SiO}_2 + [\text{La}_2\text{O}_3] + [\text{SiO}_2]$
40	60	78,4	21,6	1600	2	7,0	93,0	$2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2 + [\text{La}_2\text{O}_3 \cdot \text{SiO}_2] + [\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2]$
40	60	78,4	21,6	1650	1,5	12,0	88,0	The same
33,33	66,66	73,2	26,8	1200	8	46,0	54,0	$\text{La}_2\text{O}_3 + \text{La}_2\text{O}_3 \cdot \text{SiO}_2 + 2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2 + [\text{SiO}_2]$
33,33	66,66	73,2	26,8	1350	2	33,3	66,7	The same
33,33	66,66	73,2	26,8	1500	2	14,2	85,8	$2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{La}_2\text{O}_3 \cdot \text{SiO}_2 + [\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2] + [\text{SiO}_2]$
33,33	66,66	73,2	26,8	1600	2	4,0	96,0	$\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2 + [\text{La}_2\text{O}_3 \cdot \text{SiO}_2] + [2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2]$
33,33	66,66	73,2	26,8	1650	1,5	3,2	96,8	$\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$

\* Phases only detected in small amounts are shown in brackets.

\*\* According to crystal optical analysis the sample was one phase (orthosilicate  $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$  and  $\text{La}_2\text{O}_3$  were not detected).

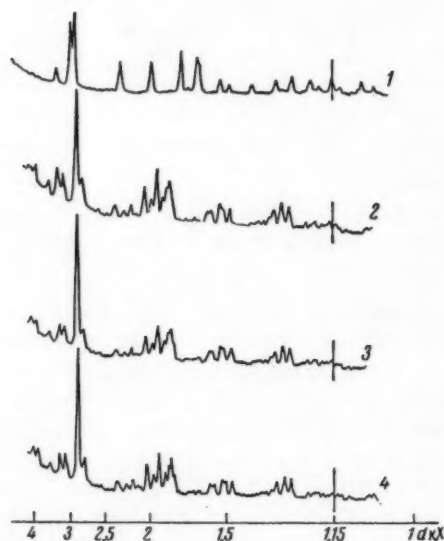


Fig. 1. X-ray diffraction patterns of lanthanum oxide and lanthanum silicate, obtained by heating for 8 hr at 1200° and subsequent treatment with ammonium nitrate. The compositions of the starting mixtures were: 1)  $\text{La}_2\text{O}_3$ , 2)  $1\text{La}_2\text{O}_3 + 1\text{SiO}_2$ , 3)  $2\text{La}_2\text{O}_3 + 3\text{SiO}_2$ , 4)  $1\text{La}_2\text{O}_3 + 2\text{SiO}_2$ .

properties. We measured the refractive indices of the silicates obtained at 1650°. The values obtained were  $n_g = 1.765$  and  $n_p = 1.755$  for the silicate of composition  $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ , and  $n_g = 1.875$  and  $n_p = 1.855$  for the silicate of composition  $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$ . These results agreed with the values obtained by Toropov and Bondar' for the refractive indices of silicates produced from melts [3].

( $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) structure, appeared in the diffraction patterns of  $1\text{La}_2\text{O}_3 + 2\text{SiO}_2$  samples which had been heated to 1500°. Complete pyrosilicate formation was observed in samples which had been heated to 1650° (Fig. 2). It is evident from Fig. 2 that, with mixtures of composition corresponding to pyrosilicate, the latter was not formed at temperatures below 1500°, and that it was only produced at high temperatures (1500-1650°) by reaction between orthosilicate and silica. With mixtures richer in silica ( $1\text{La}_2\text{O}_3 + 3\text{SiO}_2$ ), pyrosilicate formation could be observed in samples heated only to 1400°. Orthosilicate remained as an intermediate phase of the reaction. Pyrosilicate was the main phase in sample which had been heated at 1500° for 2 hr.

In the experiments with mixtures richer in lanthanum oxide ( $3\text{La}_2\text{O}_3 + 2\text{SiO}_2$ ,  $2\text{La}_2\text{O}_3 + 1\text{SiO}_2$ , and  $3\text{La}_2\text{O}_3 + 1\text{SiO}_2$ ) greatest attention was devoted to the mixture  $2\text{La}_2\text{O}_3 + 1\text{SiO}_2$ , because Wanmaker and his coauthors [5] found that the silicate  $2\text{La}_2\text{O}_3 \cdot \text{SiO}_2$  was formed at 1200-1350°. Our experiments did not confirm this, and indeed, with the composition  $2\text{La}_2\text{O}_3 + 1\text{SiO}_2$  and with mixtures richer in lanthanum oxide, x-ray analysis showed that the products were compatible with the silicates  $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$  and  $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ . Chemical and x-ray analyses showed that the excess lanthanum oxide remained in the free state.

It has already been noted that the silicates  $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$  and  $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$  gave very similar x-ray diffraction patterns. However, they differed in their crystallo-optical



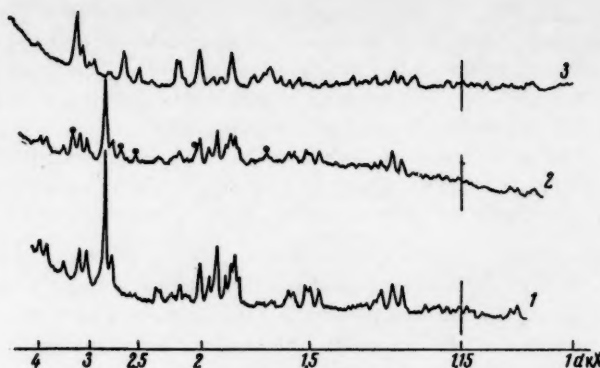


Fig. 2. X-ray diffraction patterns of samples of composition  $1\text{La}_2\text{O}_3 + 2\text{SiO}_2$  which had been heated to different temperatures for 2 hr: 1)  $1350^\circ$ , 2)  $1500^\circ$ , 3)  $1650^\circ$  (the lines marked with a dot in 2 show the start of pyrosilicate formation).

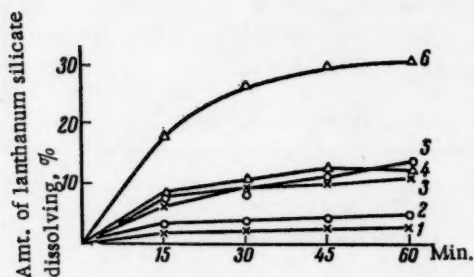


Fig. 3. The solubilities of lanthanum silicates, obtained at different temperatures, in boiling ammonium acetate solution: 1)  $1\text{La}_2\text{O}_3 + 2\text{SiO}_2$ , heated at  $1650^\circ$ ; 2)  $2\text{La}_2\text{O}_3 + 3\text{SiO}_2$ , heated at  $1600^\circ$ ; 3)  $1\text{La}_2\text{O}_3 + 2\text{SiO}_2$ , heated at  $1350^\circ$ ; 4)  $1\text{La}_2\text{O}_3 + 1\text{SiO}_2$ , heated at  $1350^\circ$ ; 5)  $2\text{La}_2\text{O}_3 + 3\text{SiO}_2$ , heated at  $1350^\circ$ ; 6)  $1\text{La}_2\text{O}_3 + 1\text{SiO}_2$ , heated at  $1650^\circ$ .

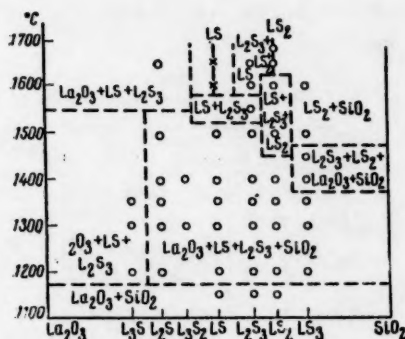


Fig. 4. The phase composition of heated mixtures of  $\text{La}_2\text{O}_3$  and  $\text{SiO}_2$  (L =  $\text{La}_2\text{O}_3$ , S =  $\text{SiO}_2$ ).

Three phases were observed in samples of original composition  $2\text{La}_2\text{O}_3 + 3\text{SiO}_2$ , with refractive indices corresponding to all of the three silicates  $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ ,  $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$ , and  $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ . Toropov and Bondar' [3] noted that the orthosilicate was unstable and decomposed into pyrosilicate and oxyorthosilicate. Our experiments confirmed this. We could not obtain orthosilicate in the pure form by reaction in the solid phase. Increasing the heating time and raising the temperature from 1500 to  $1650^\circ$ , in order to give more complete synthesis, always led to decomposition of the orthosilicate.

The lanthanum silicates obtained at  $1200$ – $1350^\circ$  were finely crystalline. Microscopic analysis of these products gave no clear results. However, we succeeded in characterizing them chemically by means of their solubilities in ammonium acetate. The silicates obtained at  $1350^\circ$  and at  $1600$  and  $1650^\circ$  showed the same stabilities towards dissolution on prolonged boiling with ammonium acetate solution. The products obtained by heating the mixtures  $1\text{La}_2\text{O}_3 + 1\text{SiO}_2$ ,  $2\text{La}_2\text{O}_3 + 3\text{SiO}_2$ , and  $1\text{La}_2\text{O}_3 + 2\text{SiO}_2$ , were subjected to prolonged treatment with boiling 20% ammonium acetate solution. They had previously been treated with the same solution to remove free lanthanum oxide. This led to partial dissolution of lanthanum silicates, particularly with products of initial composition  $1\text{La}_2\text{O}_3 + 1\text{SiO}_2$ . The orthosilicate and pyrosilicate were sparingly soluble in ammonium acetate. The products containing lanthanum silicates and unreacted silica, after removal of lanthanum oxide, were subjected to repeated treatment with ammonium acetate. The results are shown in Fig. 3. It is clear that compositions corresponding to pyrosilicate and orthosilicate, after heating at 1600 and  $1650^\circ$ , were sparingly soluble in ammonium acetate, whereas the composition corresponding

to oxyorthosilicate was appreciably soluble. The dissolution kinetics of the silicates obtained at 1350° were practically the same for all three compositions. Since, as shown above, pyrosilicate was not formed at 1350°, the reaction products must have contained only the silicates  $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$  and  $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ . Supposing that the product, obtained by heating the composition  $1\text{La}_2\text{O}_3 + 1\text{SiO}_2$  at 1350° consisted only of oxyorthosilicate, then its solubility in ammonium acetate should not have been less than that of the product from the same composition heated at 1650°. In fact it was considerably less, so it must be accepted that orthosilicate was formed with oxyorthosilicate in the product from the composition  $1\text{La}_2\text{O}_3 + 1\text{SiO}_2$  heated at 1350°; this agrees with the results of x-ray analysis. The information from all these experiments enabled us to construct a phase diagram for heated mixtures of  $\text{La}_2\text{O}_3$  and  $\text{SiO}_2$  (Fig. 4).

**Interaction of Neodymium Oxide with Silica.** The same methods of investigation were used to study the interaction of neodymium oxide with silica. The results are shown in Table 2 and Figs. 5 and 6. In order to identify the reaction products, the x-ray diffraction patterns of the products were compared with those found by Toropov and Kisel'eva [6] for neodymium silicates obtained from melts. It is clear from Table 2 that interaction had already commenced at 1200°. The appearance of a new structure was clearly visible (Fig. 5) in products which had been heated at 1300° for 2 hr, and then treated with ammonium acetate to remove neodymium oxide. The x-ray diffraction patterns of the products were very similar for the compositions  $2\text{Nd}_2\text{O}_3 + 3\text{SiO}_2$  and  $1\text{Nd}_2\text{O}_3 + 2\text{SiO}_2$ , and differed very little from that for the composition  $1\text{Nd}_2\text{O}_3 + 1\text{SiO}_2$ . All the products, independent of the oxide ratio in the initial mixture, contained the silicates  $\text{Nd}_2\text{O}_3 \cdot \text{SiO}_2$  and  $2\text{Nd}_2\text{O}_3 \cdot 3\text{SiO}_2$ . However, the reaction products obtained at 1500° differed from each other (Fig. 6). The composition  $1\text{Nd}_2\text{O}_3 + 2\text{SiO}_2$  gave pyrosilicate, still containing a small amount of the first phase, orthosilicate. In the product from the composition  $2\text{Nd}_2\text{O}_3 + 3\text{SiO}_2$  there was already some decomposition of the first-formed orthosilicate to oxyorthosilicate and pyrosilicate; the latter gave intense lines (d 3.35 and 3.06 Å) in the x-ray grams.

TABLE 2. Phase Compositions of Heated Mixtures of Neodymium Oxide and Silica

Starting mixture composition				Ignition temp., °C	Heat time, hr.	Neodymium oxide as percentage of amt. in initial mixture		X-ray analysis data
mole, %		wt., %				Soluble in $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	Combined as silicate	
$\text{Nd}_2\text{O}_3$	$\text{SiO}_2$	$\text{Nd}_2\text{O}_3$	$\text{SiO}_2$					
50	50	84,9	15,1	1200	8	75,6	24,4	$\text{Nd}_2\text{O}_3 + \text{Nd}_2\text{O}_3 \cdot \text{SiO}_2 + 2\text{Nd}_2\text{O}_3 \cdot 3\text{SiO}_2 + [\text{SiO}_2]^*$
50	50	84,9	15,1	1300	2	71,0	29,0	The same
50	50	84,9	15,1	1400	2	60,0	40,0	"
50	50	84,9	15,1	1500	2	22,7	77,3	$\text{Nd}_2\text{O}_3 \cdot \text{SiO}_2^{**} + 2\text{Nd}_2\text{O}_3 \cdot 3\text{SiO}_2 + [\text{Nd}_2\text{O}_3] + [\text{SiO}_2]$
50	50	84,9	15,1	1600	2	25,0	75,0	$\text{Nd}_2\text{O}_3 \cdot \text{SiO}_2^{**} + 2\text{Nd}_2\text{O}_3 \cdot 3\text{SiO}_2 + [\text{Nd}_2\text{O}_3]$
40	60	78,2	21,8	1200	8	62,8	37,2	$\text{Nd}_2\text{O}_3 + \text{Nd}_2\text{O}_3 \cdot \text{SiO}_2 + 2\text{Nd}_2\text{O}_3 \cdot 3\text{SiO}_2 + [\text{SiO}_2]^*$
40	60	78,2	21,8	1300	2	67,6	32,4	The same
40	60	78,2	21,8	1400	2	49,9	50,1	"
40	60	78,2	21,8	1500	2	11,3	88,7	$\text{Nd}_2\text{O}_3 \cdot \text{SiO}_2 + 2\text{Nd}_2\text{O}_3 \cdot 3\text{SiO}_2 + [\text{Nd}_2\text{O}_3 \cdot 2\text{SiO}_2]$
40	60	78,2	21,8	1600	2	17,8	82,2	The same
33,33	66,66	73,7	26,3	1200	8	85,6	14,4	$\text{Nd}_2\text{O}_3 + 2\text{Nd}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{Nd}_2\text{O}_3 \cdot \text{SiO}_2 + [\text{SiO}_2]$
33,33	66,66	73,7	26,3	1300	2	47,1	52,9	The same
33,33	66,66	73,7	26,3	1400	2	43,5	56,5	$\text{Nd}_2\text{O}_3 + 2\text{Nd}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{Nd}_2\text{O}_3 \cdot \text{SiO}_2 + [\text{Nd}_2\text{O}_3 \cdot 2\text{SiO}_2]$
33,33	66,66	73,7	26,3	1500	2	9,0	91,0	$\text{Nd}_2\text{O}_3 \cdot 2\text{SiO}_2 + [2\text{Nd}_2\text{O}_3 \cdot 3\text{SiO}_2]$
33,33	66,66	73,7	26,3	1600	2	5,5	94,5	The same

\* Phases only detected in small amounts are shown in brackets.

\*\* The absence of the phase  $2\text{Nd}_2\text{O}_3 \cdot 3\text{SiO}_2$ , in the samples heated at 1500 and 1600°, was established by measurement of refractive index.

According to the crystallo-optical measurements, the reaction product from  $1\text{Nd}_2\text{O}_3 + 1\text{SiO}_2$  at 1500-1650° was oxyorthosilicate. Similar x-ray diffraction patterns were obtained from samples of this composition which had been heated to 1300 or 1500°. Assuming that the lines d = 3.35 and 3.06 Å were not due to orthosilicate but should be attributed to the pyrosilicate structure, then it appeared that orthosilicate and oxyorthosilicate were similar from the x-ray diffraction point of view. Experiments were also carried out with mixtures of composition  $2\text{Nd}_2\text{O}_3 + 1\text{SiO}_2$ , heated for various times at 1200-1450°. The reaction products were all the same and had the composition  $1\text{Nd}_2\text{O}_3 + 1\text{SiO}_2$ . The excess of neodymium oxide remained in the free state, and could be extracted with ammonium acetate. With mixtures richer in silica, such as the compositions  $1\text{Nd}_2\text{O}_3 + 3\text{SiO}_2$  and  $1\text{Nd}_2\text{O}_3 + 2\text{SiO}_2$ , orthosilicate was also

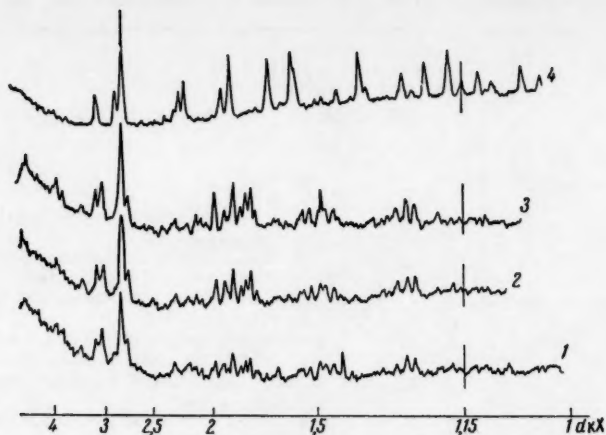


Fig. 5. X-ray diffraction patterns of neodymium silicates, obtained by heating for 2 hr at 1300°, followed by treatment with ammonium acetate: 1)  $1\text{Nd}_2\text{O}_3 + 1\text{SiO}_2$ ; 2)  $2\text{Nd}_2\text{O}_3 + 3\text{SiO}_2$ ; 3)  $1\text{Nd}_2\text{O}_3 + 2\text{SiO}_2$ ; 4)  $\text{Nd}_2\text{O}_3$ .

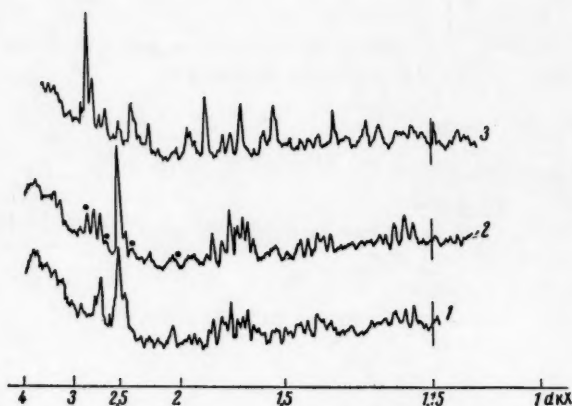


Fig. 6. X-ray diffraction patterns of neodymium silicates, obtained by heating for 2 hr at 1500°: 1)  $1\text{Nd}_2\text{O}_3 + 1\text{SiO}_2$ ; 2)  $2\text{Nd}_2\text{O}_3 + 3\text{SiO}_2$  (the lines marked with dots are due to pyrosilicate, formed by decomposition of orthosilicate); 3)  $1\text{Nd}_2\text{O}_3 + 2\text{SiO}_2$  (predominant phase pyrosilicate).

in small amounts. Only in samples of composition  $1\text{Gd}_2\text{O}_3 + 1\text{SiO}_2$ , which had been heated to 1350°, and became the main phase after heating to 1650°, though some orthosilicate remained. It is clear from these experiments that the conditions for silicate formation in the system  $\text{Gd}_2\text{O}_3\text{--SiO}_2$  were the same as in the systems  $\text{La}_2\text{O}_3\text{--SiO}_2$  and  $\text{Nd}_2\text{O}_3\text{--SiO}_2$ .

#### SUMMARY

1. By the interaction of oxides of lanthanum, neodymium, and gadolinium with silica, in the temperature range 1200–1400°, two silicates are formed together of compositions  $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$  and  $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$ , regardless of the composition of the original mixture ( $\text{La}_2\text{O}_3 : \text{SiO}_2 = 1 : 1, 2 : 3, \text{ or } 1 : 2$ ).

2. The pyrosilicates  $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$  are only formed at high temperatures (1500–1650°) in a second stage of the reaction, by interaction of the previously formed more basic silicates with silica.

formed as a primary reaction product. In distinction from the composition corresponding to pyrosilicate, the latter was detected in mixtures of composition  $1\text{Nd}_2\text{O}_3 + 3\text{SiO}_2$  which had been heated at the lower temperatures 1350–1400°. Thus the results of our experiments on the system  $\text{Nd}_2\text{O}_3\text{--SiO}_2$  showed that, under the reaction conditions used, formation of neodymium silicates was analogous to formation of lanthanum silicates.

**Interaction of Gadolinium Oxide with Silica.** In order to find out whether similar formation of silicates occurred with members of the yttrium group, we studied the interaction of silica with gadolinium oxide. Production of the gadolinium silicates was carried out as described above. The x-ray diffraction patterns of the reaction products were compared with those obtained by Toropov and Galakhov [4] in their analysis of gadolinium silicates produced from the melt. Table 3 shows the results of chemical and x-ray analyses; it is clear that gadolinium oxide reacted with silica at 1200°. The predominant phase was gadolinium oxide with all compositions below 1350°, but was orthosilicate at 1350°. Oxyorthosilicate was present in all the heated samples, but

TABLE 3. Phase Compositions of Heated Mixtures of Gadolinium Oxide and Silica

Starting mixture composition		wt., %		Ignition temp., °C	Heat time, hr.	Gadolinium oxide as percentage of amt. in initial mixture		X-ray analysis data
mole, %		Gd <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>			Soluble in NH <sub>4</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	Combined as silicate	
Gd <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Gd <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>					
50	50	85,8	14,2	1200	2	81,2	18,8	Gd <sub>2</sub> O <sub>3</sub> +2Gd <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> +{Gd <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub> }+[SiO <sub>2</sub> ] *
50	50	85,8	14,2	1300	2	63,0	37,0	The same
50	50	85,8	14,2	1350	2	57,5	42,5	2Gd <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> +{Gd <sub>2</sub> O <sub>3</sub> }+[Gd <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub> ]+[SiO <sub>2</sub> ]
50	50	85,8	14,2	1650	1,5	21,0	79,0	Gd <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub> +{2Gd <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> }+[Gd <sub>2</sub> O <sub>3</sub> ]
40	60	80,0	20,0	1200	2	88,0	22,0	Gd <sub>2</sub> O <sub>3</sub> +2Gd <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> +Gd <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub> +{SiO <sub>2</sub> }
40	60	80,0	20,0	1300	2	58,5	41,5	The same
40	60	80,0	20,0	1350	2	47,1	52,9	2Gd <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> +{Gd <sub>2</sub> O <sub>3</sub> }+[Gd <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub> ]+[SiO <sub>2</sub> ]
40	60	80,0	20,0	1650	1,5	1,8	98,2	2Gd <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> +{Gd <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub> }+[Gd <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> ]
33,33	66,66	75,3	24,7	1200	2	72,5	27,5	Gd <sub>2</sub> O <sub>3</sub> +2Gd <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> +{Gd <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub> }+[SiO <sub>2</sub> ]
33,33	66,66	75,3	24,7	1300	2	50,7	49,3	The same
33,33	66,66	75,3	24,7	1350	2	29,9	70,1	Gd <sub>2</sub> O <sub>3</sub> +2Gd <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> +Gd <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> +{SiO <sub>2</sub> }
33,33	66,66	75,3	24,7	1650	1,5	2,0	98,0	Gd <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> +{2Gd <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> }

\* Phases only detected in small amounts are shown in brackets.

3. With the compositions  $2\text{Ln}_2\text{O}_3 + 3\text{SiO}_2$ , a small amount of pyrosilicate is also formed at 1500-1650° by decomposition of the orthosilicate. The orthosilicates of lanthanum, neodymium, and gadolinium cannot be obtained in the pure state by reaction in the solid phase.

4. The crystallo-optical properties of the products, obtained by heating the compositions  $1\text{La}_2\text{O}_3 + 1\text{SiO}_2$  and  $1\text{Nd}_2\text{O}_3 + 1\text{SiO}_2$  at 1500-1650°, show that the compounds  $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$  and  $\text{Nd}_2\text{O}_3 \cdot \text{SiO}_2$  are formed.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.



## REACTIONS IN THE SOLID PHASE BETWEEN SILICA AND PRAESEODYMIUM OXIDE

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The silicates of praseodymium have not been investigated previously. It would be expected that silicates would form in the system  $\text{Pr}_2\text{O}_3\text{-SiO}_2$  by analogy with other systems containing silica and rare earth oxides [1-3].

### EXPERIMENTAL

In the present paper we report a study of the conditions for silicate formation by interaction between the praseodymium oxides  $\text{Pr}_2\text{O}_3$  and  $\text{Pr}_6\text{O}_{11}$  and amorphous silica. X-ray and chemical phase analysis were used to investigate the reaction products. The x-ray analysis was by the powder method with ionization recording. The principle of the chemical phase analysis was based on determination of the active oxygen in the praseodymium oxide which had not reacted with silica, using the method proposed by Barthauer and Pearce [4]. This analysis was carried out as follows: A 0.2 g sample was placed in a Kjeldahl flask, fitted with a reflux condenser, and dissolved by boiling with 3 N hydrochloric acid plus added potassium iodide. The cooled solution was then diluted, and the iodine produced was determined by titration with thiosulfate.

The starting materials were praseodymium oxide  $\text{Pr}_6\text{O}_{11}$  (99% pure) and amorphous silica (grade pure for analysis). The experiments were carried out in a hydrogen atmosphere and in air. For the hydrogen atmosphere we used a silit tube furnace; a stream of hydrogen was passed through from a Kipp generator. In this furnace,  $\text{Pr}_6\text{O}_{11}$  was reduced to  $\text{Pr}_2\text{O}_3$  by heating for 2 hr at  $1200^\circ$  in a hydrogen stream. Reduction was accompanied by a change in color from the black of  $\text{Pr}_6\text{O}_{11}$  to the light green of  $\text{Pr}_2\text{O}_3$ . It was shown by chemical analysis that the active oxygen content was reduced from 3.35% in the original  $\text{Pr}_6\text{O}_{11}$  to 0.1% in the reduction product. X-ray diffraction showed only the characteristic lines of the hexagonal form of  $\text{Pr}_2\text{O}_3$  (Fig. 1); the fluorite  $\text{Pr}_6\text{O}_{11}$  lattice could not be detected. If the resulting  $\text{Pr}_2\text{O}_3$  was heated in air to  $500^\circ$  and then cooled slowly, it was oxidized back to  $\text{Pr}_6\text{O}_{11}$ . This was the basis for a quantitative appraisal of the amount of praseodymia which reacted with silica in the hydrogen atmosphere, followed by oxidation of the product in air at  $450\text{-}500^\circ$ .

The mixtures used for experiment contained  $\text{Pr}_2\text{O}_3 : \text{SiO}_2$  in the ratios 1 : 1, 1 : 1.5, and 1 : 2; silicates had been obtained with these ratios in systems of silica with other rare earth oxides. The experimental results are shown in Table 1 and Fig. 1. It is clear from the data in Table 1 that the active oxygen was considerably reduced after an experiment followed by oxidation; this indicated that there had been reaction between praseodymium oxide and silica. The amount of  $\text{Pr}_6\text{O}_{11}$  which had combined as silicate could be calculated from the difference between the active oxygen contents of the original mixture and the final product. Table 1 shows that the greatest silicate yield was obtained from an initial composition  $1\text{Pr}_2\text{O}_{3.66} + 1\text{SiO}_2$ . X-ray analysis showed that the reaction product formed at  $1200^\circ$  was the same for all three initial compositions and, as established by subsequent experiments, was the orthosilicate  $2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2$ . Orthosilicate was also formed in samples heated at  $1300^\circ$ . Oxyorthosilicate was formed as well as orthosilicate when using the composition  $1\text{Pr}_2\text{O}_{3.66} + 1\text{SiO}_2$ .

Further experiments were carried out at higher temperatures in air. It is known that  $\text{Pr}_6\text{O}_{11}$  begins to dissociate when heated in air above  $450^\circ$  [5,6]. This process is reversible, and oxygen is reabsorbed on cooling. In order to find out over what temperature range the dissociation was most intense, we recorded the change in weight of a sample of  $\text{Pr}_6\text{O}_{11}$  during continuous heating up to  $1200^\circ$  and subsequent cooling. This was done by placing a pressed sample of praseodymia in a platinum cup, which was suspended inside a tube furnace from a torsion balance. The heating curve (Fig. 2) showed steps, indicating that the dissociation process took place in steps. The cooling curve also showed indications of steps. There was a loss of 2.9% of oxygen at  $1200^\circ$ .

TABLE 1. Phase Compositions of Mixtures of  $\text{Pr}_6\text{O}_{11}$  and  $\text{SiO}_2$  Heated in a Hydrogen Atmosphere

Initial mixture composition				Ignition temperature, °C	Heating time, hr.	Active oxygen content, %		Reacted preaseodymium oxide, %	X-ray analysis results
Mole ratio		Wt., %							
Pr <sub>2</sub> O <sub>3</sub> ·n	SiO <sub>2</sub>	Pr <sub>2</sub> O <sub>3</sub> ·n	SiO <sub>2</sub>						
1	1	85	15	1200	2	2,85	2,36	17,2	Pr <sub>2</sub> O <sub>3</sub> +2Pr <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>
1	1	85	15	1200	5	2,85	1,20	57,8	The same
1	1	85	15	1300	2	2,85	1,15	59,5	Pr <sub>2</sub> O <sub>3</sub> +2Pr <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> +Pr <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub> +{SiO <sub>2</sub> }
1	1,5	79,1	20,9	1200	2	2,66	1,93	27,8	Pr <sub>2</sub> O <sub>3</sub> +2Pr <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>
1	1,5	79,1	20,9	1200	5	2,66	0,85	68,0	The same
1	1,5	79,1	20,9	1300	2	2,66	0,70	73,7	Pr <sub>2</sub> O <sub>3</sub> +2Pr <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> +{SiO <sub>2</sub> }
1	2	73,9	26,1	1200	2	2,47	1,77	28,4	Pr <sub>2</sub> O <sub>3</sub> +2Pr <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>
1	2	73,9	26,1	1200	5	2,47	0,70	71,5	The same
1	2	73,9	26,1	1300	2	2,47	0,65	73,8	Pr <sub>2</sub> O <sub>3</sub> +2Pr <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> +SiO <sub>2</sub>

\* Phases only detected in small amounts are shown in brackets.

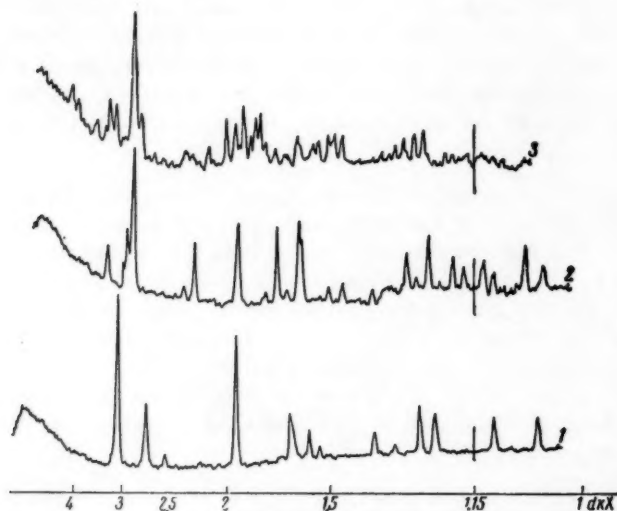


Fig. 1. X-ray diffraction patterns of praseodymium oxide and silicate, obtained by heating for 5 hr in a hydrogen atmosphere at 1200°: 1)  $\text{Pr}_6\text{O}_{11}$ ; 2)  $\text{Pr}_2\text{O}_3$ ; 3)  $2\text{Pr}_2\text{O}_3 + 3\text{SiO}_2$ .

A complex thermal analysis of  $\text{Pr}_6\text{O}_{11}$  was carried out with the equipment constructed by Keler and Kuznetsov [7]. The heating rate was 13° per min, but the cooling rate was not uniform: from 1500 to 1200° took 15 min, from 1200 to 900° 25 min, and from 900 to 400° 1.5 hr. The test sample was heated to 500° before carrying out the analysis, in order to decompose any oxalate impurity. It is clear from Fig. 3 that the differential heating curve showed four endothermic effects attributable to dissociation of praseodymium oxide. The loss of oxygen was also evident in the thermogravimetric curve for change in weight of the sample. The active oxygen contents of the dissociation products were determined by chemical analysis. In order to do this, samples of praseodymium oxide were heated in a tube furnace at the same heating rate as was used in the thermal analysis, and quenched at the temperatures 600, 850 and 1200°. The sample quenched at 600° contained 2.70% of oxygen, corresponding with the results of the thermogravimetric analysis. The samples quenched at 850 and 1200° contained 2.51 and 2.09% respectively of active oxygen, results which did not agree with the thermogravimetric curve. Evidently, quenching at these temperatures did not produce stable phases. X-ray analyses of these samples showed that they contained the fluorite lattice character-

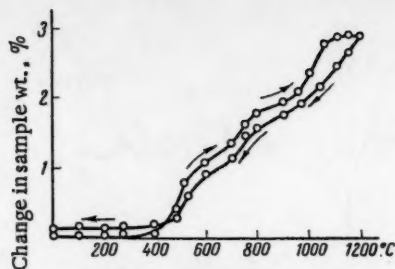


Fig. 2. Thermogravimetric curve for praseodymium oxide.

istic of the oxide  $\text{Pr}_6\text{O}_{11}$ . The dilatometric curve of the thermogram shows that dissociation was accompanied by a slight extension of the sample up to 900°, followed by an intense contraction amounting to 25% at 1500°.

The differential cooling curve showed five exothermic effects, attributable to oxygen absorption, and there was a corresponding gain in weight of the sample. At the end of the thermal analysis, the sample contained 2.9% of active oxygen, somewhat less than the original 3.35%. The thermogram shows that oxygen absorption was accompanied by a considerable extension of the sample in the temperature range 1100-1000°. Except for the first one, the endothermic effects did not occur at the same temperatures as the exothermic effects; this could be due to hysteresis, to the conditions for carrying out the thermal analysis, or to a number of other factors. The problem of the behavior of praseodymium oxide on heating and the appearance of phases impoverished with respect to oxygen, which are stable under definite temperature conditions, requires a more detailed investigation which is outside the range of this paper.

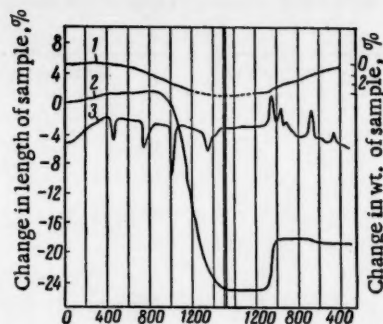


Fig. 3. Thermogram of praseodymium oxide: 1) gravimetric curve; 2) dilatometric curve; 3) differential heating curve.

TABLE 2. The Phase Compositions of Mixtures of  $\text{Pr}_6\text{O}_{11}$  with  $\text{SiO}_2$ , Heated in Air

Initial mixture composition		Ignition temperature, °C	Heating time, hr.	Active oxygen content, %			Results of x-ray analysis
Mole ratio	Wt., %			In initial mixture	After experiment	Reacted $\text{Pr}_6\text{O}_{11}$ , %	
$\text{Pr}_6\text{O}_{11}$	$\text{SiO}_2$						
1	1	85,0	15,0	1200	2	2,85	$2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2 + 2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{Pr}_2\text{O}_3 \cdot \text{SiO}_2$
1	1	85,0	15,0	1200	24	2,85	The same
1	1	85,0	15,0	1200	48	2,85	$\text{Pr}_2\text{O}_3 \cdot \text{SiO}_2 + 2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{Pr}_2\text{O}_3 \cdot \text{SiO}_2 + [\text{SiO}_2]^*$
1	1	85,0	15,0	1400	2	2,85	$\text{Pr}_2\text{O}_3 \cdot \text{SiO}_2 + \text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2 + [2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2]$
1	1	85,0	15,0	1600	2	2,85	$\text{Pr}_2\text{O}_3 \cdot \text{SiO}_2 + [2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2]$
1	1	85,0	15,0	1650	2	2,85	$\text{Pr}_2\text{O}_3 \cdot \text{SiO}_2$
1	1,5	79,1	20,9	1200	2	2,66	$\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2 + 2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2$
1	1,5	79,1	20,9	1200	24	2,66	The same
1	1,5	79,1	20,9	1200	48	2,66	$2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2 + [\text{SiO}_2]$
1	1,5	79,1	20,9	1400	2	2,66	$\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2$
1	1,5	79,1	20,9	1600	2	2,66	$2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{Pr}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{Pr}_2\text{O}_3 \cdot \text{SiO}_2$
1	1,5	79,1	20,9	1650	2	2,66	The same
1	2	73,9	26,1	1200	2	2,47	$\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2 + 2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2$
1	2	73,9	26,1	1200	24	2,47	The same
1	2	73,9	26,1	1200	48	2,47	The same
1	2	73,9	26,1	1400	2	2,47	$2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{Pr}_2\text{O}_3 \cdot 2\text{SiO}_2 + [\text{SiO}_2]$
1	2	73,9	26,1	1600	2	2,47	$\text{Pr}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2$
1	2	73,9	26,1	1650	2	2,47	$\text{Pr}_2\text{O}_3 \cdot 2\text{SiO}_2$
2	1	91,8	8,2	1200	2	3,07	$\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{Pr}_2\text{O}_3 \cdot \text{SiO}_2$
2	1	91,8	8,2	1350	16	3,07	The same
2	1	91,8	8,2	1350	8	3,07	The same
1	3	65,5	34,5	1300	4	2,19	$2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{SiO}_2$
1	4	58,7	41,3	1350	3	1,97	$2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{Pr}_2\text{O}_3 \cdot 2\text{SiO}_2 + [\text{SiO}_2]$

\* Phases only present in small amounts are shown in brackets.

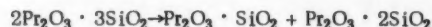
TABLE 3. Densities and Melting Points of Praeseodymium Silicates

Compound	Density	Melting point, °C
$\text{Pr}_2\text{O}_3 \cdot \text{SiO}_2$	5.89	1890
$2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2$	5.33*	1860*
$\text{Pr}_2\text{O}_3 \cdot 2\text{SiO}_2$	5.08	1830

\* The orthosilicate may have contained its decomposition products, pyrosilicate and orthosilicate.

For the production of praeseodymium silicates, samples of mixtures of  $\text{Pr}_6\text{O}_{11}$  with silica were pressed into tablets and heated at temperatures from 1200-1650° in silit, cryptol, or flame furnaces. A tablet of praeseodymium oxide was heated together with the mixture sample in each experiment. The active oxygen contents of the samples were determined after heating. There was no change in the active oxygen content of  $\text{Pr}_6\text{O}_{11}$  after it had been heated in air to 1400° and cooled gradually, but it was reduced from 3.35 to 3.0-2.9% after heating to 1500-1600°. The results of x-ray and chemical analysis of the ignited samples are shown in Table 2; it is clear that praeseodymium oxide began to react with silica to give silicate in an atmospheric medium, even at 1200°.

Orthosilicate  $2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2$  was the reaction product from the compositions  $2\text{Pr}_2\text{O}_{3.66} + 3\text{SiO}_2$  and  $\text{Pr}_2\text{O}_{3.66} + 2\text{SiO}_2$ , as in the experiments carried out in a hydrogen medium. Oxyorthosilicate  $\text{Pr}_2\text{O}_3 \cdot \text{SiO}_2$  was formed with orthosilicate from the composition  $1\text{Pr}_2\text{O}_{3.66} + 1\text{SiO}_2$ . Only oxyorthosilicate was formed from the mixture richer in praeseodymium oxide,  $2\text{Pr}_2\text{O}_{3.66} + 1\text{SiO}_2$ . There was a decrease in the active oxygen and an increase in the oxyorthosilicate content when the composition  $1\text{Pr}_2\text{O}_{3.66} + \text{SiO}_2$  was heated to higher temperatures, and, after heating to 1650°, the product was almost pure oxyorthosilicate with very slight contamination by orthosilicate. The composition  $2\text{Pr}_2\text{O}_{3.66} + 3\text{SiO}_2$  showed decreasing active oxygen content with increasing ignition time and ignition temperature; x-ray analysis showed only one orthosilicate in a sample heated to 1400°. In this case, chemical analysis showed that there was still some unreacted praeseodymium oxide. The orthosilicate was unstable at higher temperatures and decomposed in accordance with the equation:



A similar phenomenon, decomposition of orthosilicates in the temperature range 1400-1650°, has been observed with other rare earth element silicates.

TABLE 4. Interplanar Spacings of Praeseodymium Silicates

$\text{Pr}_2\text{O}_3 \cdot \text{SiO}_2$		$2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2$		$\text{Pr}_2\text{O}_3 \cdot 2\text{SiO}_2$		$\text{Pr}_2\text{O}_3 \cdot \text{SiO}_2$		$2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2$		$\text{Pr}_2\text{O}_3 \cdot 2\text{SiO}_2$	
d/n	I/I <sub>0</sub>	d/n	I/I <sub>0</sub>	d/n	I/I <sub>0</sub>	d/n	I/I <sub>0</sub>	d/n	I/I <sub>0</sub>	d/n	I/I <sub>0</sub>
4.38	30	4.10	20	3.37	100	1.74	41	1.87	40	1.792	15
3.74	10	3.90	18	3.26	35	1.71	10	1.83	27	1.712	25
3.20	84	3.47	11	3.14	19	1.688	16	1.804	30	1.661	40
3.14	35	3.20	30	3.07	25	1.662	41	1.784	37	1.631	15
2.99	18	3.15	29	2.86	20	1.651	33	1.756	17	1.601	17
2.93	61	3.10	15	2.69	33	1.602	12	1.643	11	1.560	12
2.87	65	2.84	100	2.64	29	1.584	27	1.556	14	1.504	12
2.81	100	2.78	37	2.49	27	1.536	27	1.533	16	1.453	12
2.71	20	2.74	20	2.16	33	1.394	18	1.497	10	1.410	12
2.29	10	2.70	14	2.14	27	1.319	14	1.479	16	1.364	20
2.16	55	2.28	11	2.10	15	1.283	12	1.454	17	1.351	15
2.01	57	2.15	13	2.02	67	1.267	16	1.341	11	1.318	23
1.94	65	2.10	13	1.98	17	1.254	20	1.323	11	1.283	21
1.90	33	1.99	20	1.926	21	1.234	12	1.304	13	1.262	13
1.84	22	1.97	30	1.882	30	1.205	16	1.287	17	1.248	20
1.79	18	1.92	33	1.821	50	1.179	12	1.263	27	1.223	15
								1.244	22	1.159	24

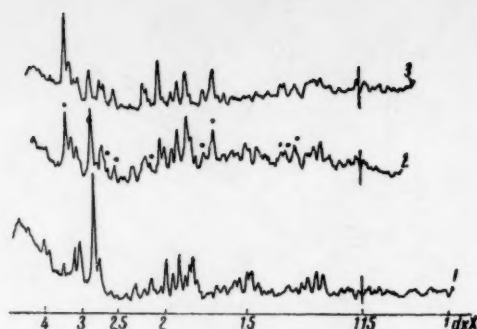


Fig. 4. X-ray diffraction patterns of praeseodymium silicates obtained from the mixture  $1\text{Pr}_2\text{O}_{3.66} + 2\text{SiO}_2$  at different temperatures: 1) 1200° for 24 hr; 2) 1400° for 2 hr; 3) 1600° for 2 hr. The lines marked with dots in 2 are due to pyrosilicate.



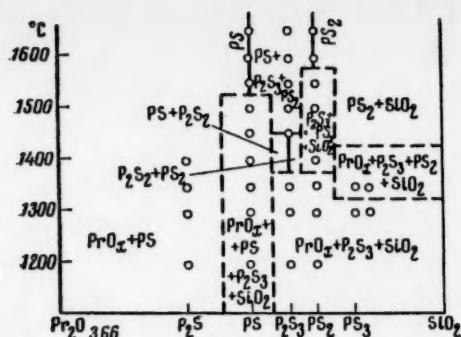


Fig. 5. The phase compositions of ignited mixtures of praseodymium oxide with silica, where  $\chi \leq 1.83$ ; P =  $\text{Pr}_2\text{O}_{3.66}$  and S =  $\text{SiO}_2$ .

diagram for this system, covering the temperature range 1200-1650° (Fig. 5).

Orthosilicate was formed first from the composition  $1\text{Pr}_2\text{O}_{3.66} + 2\text{SiO}_2$ ; pyrosilicate could only be observed after heating to 1400°, and orthosilicate still remained the predominant phase (Fig. 4). The orthosilicate content decreased with further rise in ignition temperature, and pyrosilicate was the only product after heating to 1650°. With compositions richer in silica,  $1\text{Pr}_2\text{O}_{3.66} + 3\text{SiO}_2$  and  $1\text{Pr}_2\text{O}_{3.66} + 4\text{SiO}_2$ , orthosilicate was also the primary reaction product, but pyrosilicate began to form already after heating to 1300°. Such a subsequent production of pyrosilicate (formed by a second stage of the reaction) is also characteristic of other systems of rare earth oxides with silica, in the solid phase.

We measured the melting points and densities, and calculated the interplanar spacings, for the silicates which we synthesized. The results are shown in Tables 3 and 4.

The information from all these experiments on the interaction of praseodymium oxide with silica enabled us to construct a phase

#### SUMMARY

1. Silicates of composition  $\text{Pr}_2\text{O}_3 \cdot \text{SiO}_2$ ,  $2\text{Pr}_2\text{O}_3 \cdot 3\text{SiO}_2$ , and  $\text{Pr}_2\text{O}_3 \cdot 2\text{SiO}_2$  are formed by the interaction of praseodymium oxide with silica.
2. The silicates can be obtained by interaction of silica with  $\text{Pr}_6\text{O}_{11}$  in an atmosphere of hydrogen or of air.
3. At 1200-1300° in an atmosphere of hydrogen or air, orthosilicate is formed as the predominant reaction product phase, regardless of the ratio of praseodymium oxide to silica in the initial mixture within the range 1 : 1, 2 : 3, and 1 : 2. The orthosilicate is unstable at the higher temperatures 1400-1650° and decomposes into the silicates  $\text{Pr}_2\text{O}_3 \cdot \text{SiO}_2$  and  $\text{Pr}_2\text{O}_3 \cdot 2\text{SiO}_2$ .
4. The pyrosilicate  $\text{Pr}_2\text{O}_3 \cdot 2\text{SiO}_2$  is formed at 1400-1650° in a secondary stage of the reaction, by interaction of more basic praseodymium silicates with silica. The oxyorthosilicate  $\text{Pr}_2\text{O}_3 \cdot \text{SiO}_2$ , slightly contaminated with orthosilicate, can be produced at 1600-1650°.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

## PHYSICAL CHEMISTRY

### AN INVESTIGATION OF THE STRUCTURE AND REACTIVITY OF SOME STABLE RADICALS

A REPORT OF THE GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCE ,  
THE ACADEMY OF SCIENCES OF THE USSR, MOSCOW, JUNE 22, 1961

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More than sixty years ago Gomberg showed that the dissociation of hexaphenylethane forms triphenylmethyl, a free radical in thermodynamic equilibrium with its dimer [1]. The equilibrium concentration of triphenylmethyl depends on the temperature and on other factors. Many thermodynamically stable radicals were studied in the following years. It was considerably later that stable radicals were produced by chemical reaction, for example, by the removal of one hydrogen atom from a molecule. Müller and Ley and Becconsall, et al. [2,3] produced a series of phenoxyl radicals in this way. These radicals are not in thermodynamic equilibrium, and their stability is associated with steric hindrance. Stable radicals of this class can therefore be called kinetically stable radicals. Since the life-time of stable radicals is large in comparison with the duration of the majority of physical experiments and chemical processes, one can treat stable radicals like ordinary molecules.

During the past fifty years a larger and larger role has been ascribed to short-lived free radicals in the mechanism of homogeneous and heterogeneous chemical reactions; interest in the investigation of the physical and chemical properties of radicals has therefore rapidly increased. Nevertheless, present knowledge of the thermodynamically stable and kinetically stable radicals is extremely small. Thus, in Reutov's book "Theoretical Problems of Organic Chemistry" [4], of 58 pages devoted to free radicals only 10 pages are granted to thermodynamically stable radicals and not even one page to kinetically stable free radicals. The discovery by Zavoiskii of electron paramagnetic resonance (EPR) has played a large role in the development of free radical investigation; radicals in comparatively small concentrations [5] may be observed and identified by this means. This method has been widely developed in the USSR thanks to the labors of Voevodskii and his students who developed and warranted the mass production of native apparatus [6].

New information about stable radicals: their structures, physical properties, and chemical reactions are set forth in the present article. In collaboration with Razuvaev, Khidekel' and Gorbunova we have studied by the EPR method the radical synthesized by Pummerer as an example of a thermodynamically stable radical; it results from the reversible dissociation of the following peroxide:

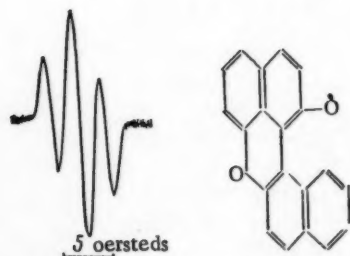
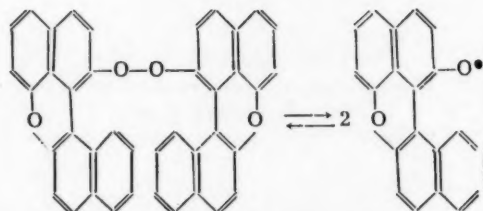


Fig. 1. The EPR signal of the radical.



The EPR spectrum of this radical is depicted in Fig. 1. The triplet structure of the spectrum shows the delocalization of the unpaired electron which interacts with two protons of the aromatic ring. On lowering the temperature

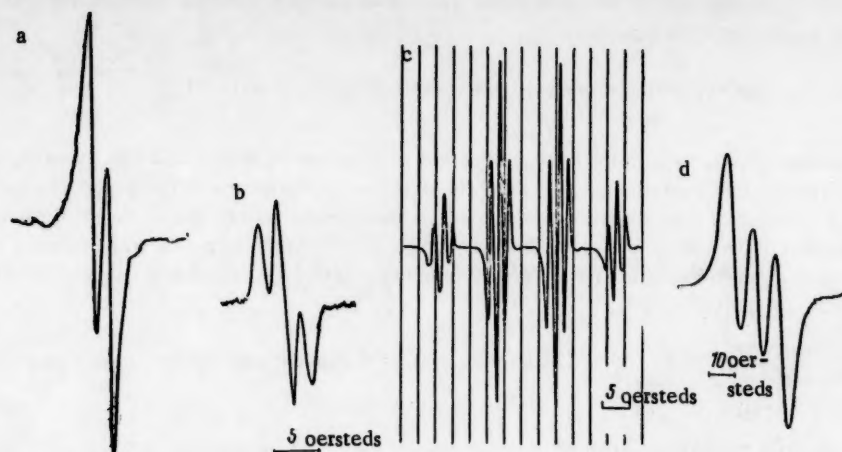
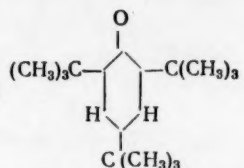


Fig. 2. The EPR signals of the radicals obtained: a) by gamma irradiation of polyformaldehyde (dose of  $\gamma$  rays  $25 \times 10^6$  roentgens); b) by the oxidation of tritertiarybutylphenol; c) by the oxidation of ionol; d) by the oxidation of diphenylamine (the diaphenylnitrogen radical).

from  $-10$  to  $-60^\circ$  the equilibrium concentration of the free-radical regularly diminishes, so that the equilibrium constant of the dissociation reaction of the peroxide may be calculated. The value found is  $1.8 \times 10^{29} \exp(-16500/RT)$   $\text{cm}^{-3}$ . The O-O bond energy in this peroxide, 16500 cal/M, is very low, which explains the considerable degree of dissociation of the peroxide even at low temperatures.

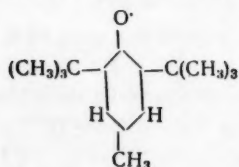
We obtained kinetically stable radicals by the oxidation of derivatives of phenols and secondary aromatic amines with organic peroxides, percarbonates, or  $\text{PbO}_2$  in benzene or toluene solutions. The solutions of the radicals are colored; after evaporation of the solvent some of the radicals formed colored crystals. We prepared more than 40 kinetically stable radicals - substituted phenoxy and diarylamines; their EPR spectra are characterized by a fine structure caused by the interaction of the electron's spin with the magnetic moment of the hydrogen and nitrogen nuclei. If the magnetic moment of the unpaired electron interacts with one proton only, the spin of which is equal to  $\frac{1}{2}$ , then a doublet is observed in the EPR spectrum of the radical; an example of this is polyformaldehyde irradiated with gamma rays. The radical  $\sim\text{O}-\text{CH}-\text{O}\sim$  is formed in this case; its EPR spectrum is depicted in Fig. 2,a. The relative intensities of the doublet are 1 : 1 and the magnitude of the splitting is 15 oersteds.

By the oxidation of tritertiarybutylphenol the kinetically stable radical



is formed, so-

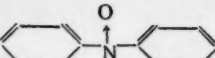
lutions and crystals of which are colored blue. The unpaired electron in this radical interacts with the two meta-hydrogens of the benzene ring, and the EPR spectrum therefore has a triplet structure which is depicted in Fig. 2,b. The magnitude of the splitting in this case is 1.7 oersteds, which shows the comparatively small spin density in the meta positions of the nucleus. The oxidation of 2,6-ditertiarybutyl-4-methylphenol (ionol) forms the radical



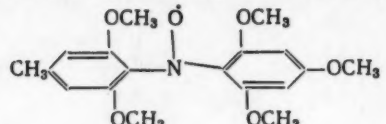
, which is yellow in color; the unpaired electron here interacts with the three hydrogen atoms

of the methyl group in the para-position so that a quadruplet is observed in the spectrum with relative intensities 1 : 3 : 3 : 1; the magnitude of the splitting is 10.7 oersteds. Because of the weaker interactions with the two meta-hydro-

gen atoms of the benzene ring each of the lines of the quadruplet are split into three components with relative intensities 1 : 2 : 1, as is apparent from Fig. 2,c.

The oxidation of diphenylamine forms the radical diphenyl nitrogen oxide (I) , the un-

paired electron of which interacts with the nitrogen nucleus with its spin of unity. The EPR spectrum depicted in Fig. 2,d therefore contains a triplet. In dilute solutions of the diphenyl nitrogen each of the triplet lines is split into 15 components with a splitting of approximately 0.5 oersteds, which is explained by the weak interactions of the unpaired electron with the non-equivalent protons of the benzene rings. The EPR spectrum of a dilute solution of the diphenyl nitrogen in toluene is given in Fig. 3,a. We were able to record a still larger number of lines in the EPR spectrum of

the radical  (Fig. 3,b). The delocalized electron in this case interacts with the

nitrogen nucleus and with the hydrogen nuclei of the benzene ring and of the methoxy groups.

All of the radicals discussed above disappear very slowly at room temperature and in the absence of oxygen so that it is possible to investigate their physical and chemical properties. Some of the radicals can easily be distilled without decomposition at a temperature of approximately 100° in vacuo; they are crystallized on cold surfaces where they can be determined by the EPR method.

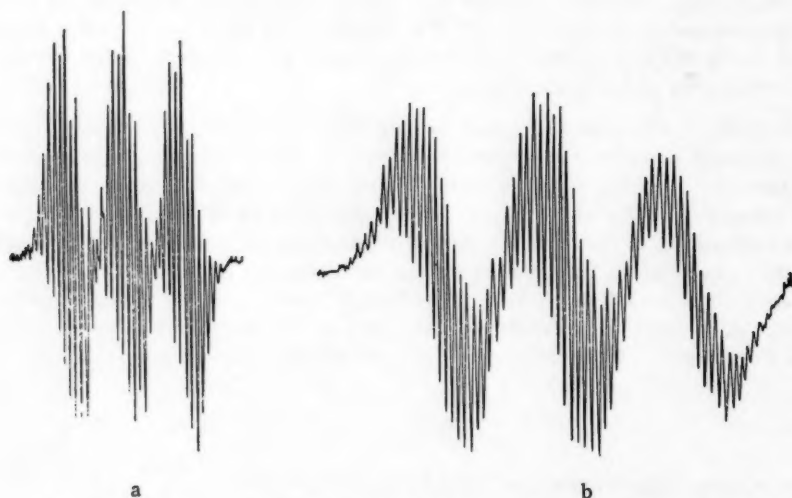
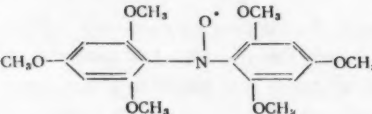


Fig. 3. The structure of the EPR signal of dilute solutions of: a) the diphenyl ni-

trogen (hyperfine structure); b) of the radical  (fine structure).

In collaboration with É.G. Gintsberg and B.M. Kovarskaya we determined the absorption spectra of some of the kinetically stable radicals in the ultra-violet region. The spectra of the molecules and the radicals obtained from them by oxidation are both depicted in Fig. 4 for comparison. The formation of the radicals displaces the absorption bands from the ultra-violet to the visible region, which explains the color of the solutions and crystals of the radicals. The absorption spectra of some of the radicals were also determined in the infra-red region. For example, the infra-red absorption spectra of ionol and its radicals are given in Fig. 5. It is apparent from the figure that the partial formation of the radical decreases the intensity of the hydroxyl absorption band at 2.8 microns, and that new bands appear in the 6.2  $\mu$  region.

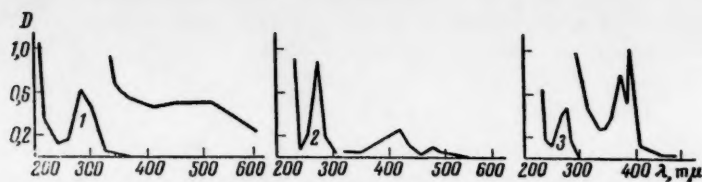


Fig. 4. The ultra-violet and visible absorption spectra of the molecules and their radicals: 1) the diphenyl nitrogen; 2) ionol; 3) tritertiarybutylphenoxyl.

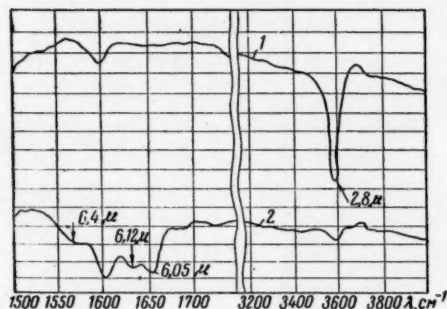


Fig. 5. The infra-red absorption spectra of: 1) the ionol molecule; 2) the ionol radical.

In collaboration with Gintsberg and Kovarskaya we showed that the kinetically stable radicals can be polarographically reduced in alcoholic solutions in the presence of LiCl in the potential region 0.35-0.45 V. Three examples are depicted in Fig. 6: polarograms of the reduction of the radical (1) and of two phenoxyl radicals. It is interesting to observe that if the radical contains a polarographically active group, the free valence and the active group can be reduced independently of one another at their respective potentials.

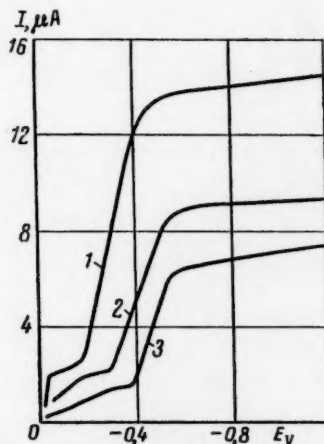
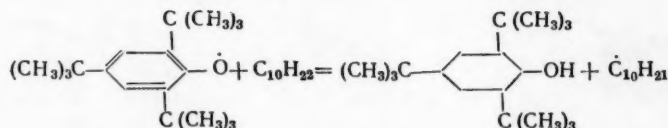


Fig. 6. Polarograms of the reduction of the radicals: 1) the diphenyl nitrogen; 2) ionol; 3) tritertiarybutylphenoxyl.

The kinetically stable radicals which we have studied are not able to dimerize, apparently because of steric hindrance; however they can remove hydrogen from other molecules, for example from the solvent, in this way reforming the original phenol. We investigated the kinetics of the reaction of tritertiarybutylphenoxyl with *n*-decane in the absence of oxygen over the temperature interval 90 to 150°. The experiments showed that the reaction



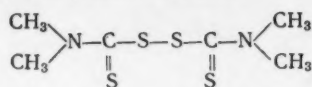
is described by a second-order equation with the constant

$$k = 4 \cdot 10^{-10} \exp(-27500/RT) \text{ cm}^3 \cdot \text{sec}^{-1}$$

We also observed by the EPR method the kinetics in solution of a series of reactions between the kinetically



stable radicals and molecules of various substances. As an example we cite the reaction of the addition of the radical (I) to the sulfur of the molecule of tetramethylthiuramdisulfide



which we studied in collaboration with M.S. Khlopyankina. In carrying out this reaction we recorded the EPR spectrum depicted in Fig. 7. The triplet with g-factor equal to 2.0065 corresponds to the radical (I); the formation of the triplet with g-factor 2.030, for which a sulfur radical is responsible can be explained as arising from the N-S bond. It has not been possible to isolate and establish the structure of the secondary complex radical formed as a result of the reaction.

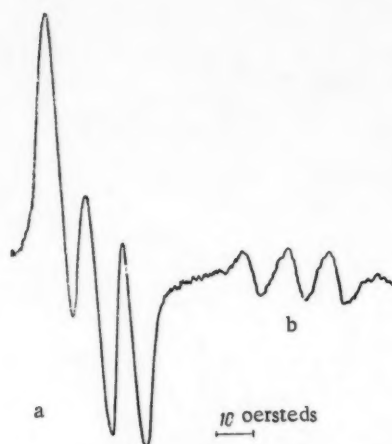


Fig. 7. The EPR spectrum of the primary radical from the diphenyl nitrogen (a); and the product of its addition to tetramethylthiuramdisulphide.

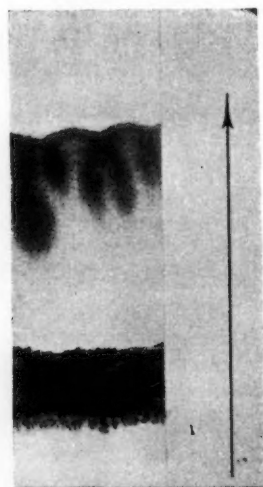
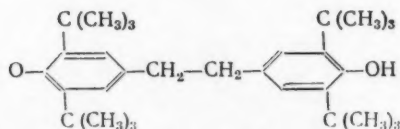


Fig. 8. The chromatographic separation of a mixture of two radicals.

The task of separating the kinetically free radicals from one another is very important in working with them. We have shown that in numerous cases this problem can be aided by chromatography. For example, consider the separation of the primary and secondary radicals which are formed during the protracted oxidation of ionol in toluene solution. The complex EPR signal which is obtained from the oxidation product makes it necessary to assume the presence of a mixture of radicals in the solution. If the solution is applied in the form of a band on chromatographic paper, and the band is dried the immersion of the edge of the paper in ethyl alcohol will cause the formation of the chromatogram depicted in Fig. 8. One can easily see that the mixture of colored radicals has been separated. One of the components moves with the alcohol front with  $R_f = 1$ , but the other remains practically unmoved so that  $R_f = 0$ . The first radical is yellow, the second orange. We determined the EPR spectra of the colored parts of the chromatogram separately. The spectrum of the first radical coincided with the spectrum of the ionol radical depicted in Fig. 2,c, but the spectrum of the second radical, given in Fig. 9, has a doublet structure. If crystals of the second radical which is separated on the paper are dissolved in toluene the EPR spectrum of this solution has a triplet structure with a fine splitting of each of the lines into three with relative intensities 1 : 2 : 1 (Fig. 9,b). The doublet EPR spectrum depicted in Fig. 8,a is again obtained when this solution is frozen. Thus our radical has a doublet spectrum in the solid phase, but its spectrum is a triplet of triplets in solution.

The regularities which are observed find an explanation if one assumes that the strong oxidation of ionol forms the radical



Because of the doubled molecular weight and the presence of a hydroxyl group this radical is more strongly adsorbed

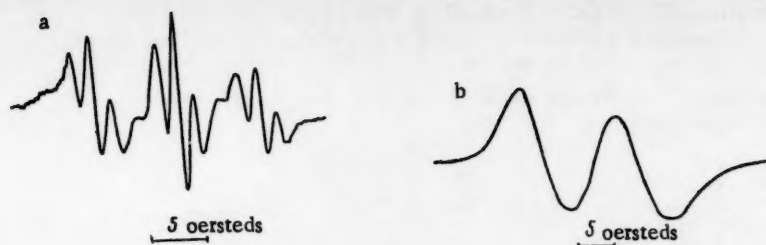
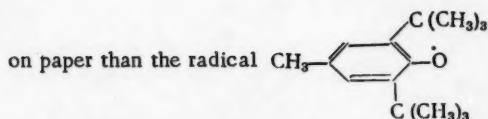


Fig. 9. EPR spectra: a) the radical  $\dot{\text{O}}-\text{C}_6\text{H}_2(\text{C}(\text{CH}_3)_3)_2-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_2(\text{C}(\text{CH}_3)_3)_2-\text{OH}$  in crystalline form; b) the radical  $\dot{\text{O}}-\text{C}_6\text{H}_2(\text{C}(\text{CH}_3)_3)_2-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_2(\text{C}(\text{CH}_3)_3)_2-\text{OH}$  in solution.



and therefore is characterized by a smaller  $R_f$  value. Compara-

tively rapid rotation of the  $\text{CH}_2$  groups takes place around the C-C aryl-alkyl bonds in solutions of this radical, so that both hydrogens can interact with the unpaired electron to form a triplet with a splitting of 8 oersteds. The lines of the triplet are split because of the interaction of the electron with the meta-hydrogens of the benzene rings. On crystallization or the formation of a solid solution the rotation of the  $\text{CH}_2$  groups becomes impossible, and the unpaired electron interacts only with one of the hydrogens of the  $\text{CH}_2$  group, resulting in the formation of a doublet signal. It should be mentioned that the formation of the molecule which we have proposed with the "bionol" structure has been previously observed in the oxidation of ionol [7].

We hope that this direction which we have pursued, and which we have tried to present in the present article will help to broaden significantly the chemistry of the free radicals, this rapidly developing important division of organic chemistry.

#### SUMMARY

1. The stable radicals from 40 antioxidants (substituted phenols and aromatic amines) were obtained by oxidation. The EPR spectra of these radicals were investigated.
2. These radicals can remove hydrogen from solvents. The kinetics of this reaction were studied at various temperatures. In this way these radicals can serve as a medium for the investigation of the reactivity of various bonds.
3. The absorption spectra of some of the antioxidants and their radicals were taken in the ultraviolet and infra-red regions.
4. The radicals obtained by the oxidation of ionol were separated and identified by paper chromatography.
5. A classification of stable radicals is suggested.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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POLAROGRAPHIC STUDY OF THE EFFECT OF TEMPERATURE  
ON THE PROTONATION RATE OF THE MALEIC ACID DI-ANION

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The kinetic and catalytic currents, as was shown in Refs. [1 and 2], are usually the sum of two currents, caused by one and the same chemical reaction, which precedes the electrode reaction, and occurs in the volume of the solution and on the surface of the electrode. One of the few exceptions is the kinetic current, which is limited by the recombination of the maleic acid di-anion with proton donors which occurs only in the volume of the solution [2]. In this case the rate content of the preceding chemical reaction may be calculated by Koutecky's method [3]. Previously, in Ref. [2], we made a detailed study of the kinetics of interaction of the maleic acid di-anion with various proton donors. The present paper gives a study of the temperature dependence of some of these reactions, found from the energy and entropy of activation.

EXPERIMENTAL

The polarographic studies were made at 15, 25, 35, and  $45^\circ \pm 0.1^\circ$  in a thermostatically controlled cell [4]. The anode was an attached saturated calomel electrode [4]. The drop electrode was provided with a pusher for forcing off the drop, [5], and had  $m$  and  $t$  values, respectively, as follows: at  $15^\circ$ , 1.415 mg/sec and 0.31 sec; at  $25^\circ$ , 1.460 mg/sec and 0.30 sec; at  $35^\circ$ , 1.505 mg/sec and 0.29 sec; and at  $45^\circ$ , 1.550 mg/sec and 0.28 sec. At  $25^\circ$ ,  $m^{2/3}t^{1/6} = 1.050 \text{ mg}^{2/3}/\text{sec}^{-1/2}$ . The polarograms were taken on a TSLA Énergohermet electronic polarograph [6]. The limiting current values were corrected for residual current, for which purpose curves were taken of the background of every solution. The concentration of maleic acid in the solution studied was  $5.70 \cdot 10^{-5}$ – $5.76 \cdot 10^{-4}$  M/l. Borate phosphate veronal and ammonium buffer solutions over the range pH 8–10 were used in the work, which were prepared in the same way as in Ref. [2].

To find the rate constant for the reaction of the maleic acid di-anion with individual acids the currents were studied in solutions with constant pH, but a different concentration of the buffer components. The ionic strength in all cases was reduced to  $\mu = 1.0$ , by adding KCl. Usually the pH of the solutions was verified not only during preparation, but after taking the polarograms. The pH measurement was made in a thermostatically controlled cell at a fixed temperature, using a glass electrode with an LP-5 potentiometer. As pH comparison standards at different temperatures, borate buffer solutions were used, for which the temperature dependence of the pH was accurately known [7]. The characteristic of the glass electrode, i.e.,  $\Delta\text{pH}/\Delta E$  at different temperatures was determining by measuring the pH of standard borate and phthalate buffer solutions. For the latter the change of pH with temperature is also known [8]. To calculate the rate constant (see below) it is necessary to know the second dissociation constant of maleic acid ( $K''_{MA}$ ). These were measured potentiometrically, but titrating 0.1 M solution of acid with 0.1 M KOH solution at ionic strength  $\mu = 1.0$  (adding KCl). Here the values obtained were:  $K''_{MA} = 3.16 \cdot 10^{-6}$ ,  $3.2 \cdot 10^{-6}$ ,  $2.92 \cdot 10^{-6}$  and  $2.82 \cdot 10^{-6}$  at 15, 25, 35 and  $45^\circ$  respectively.

In view of the large discrepancies existing in the literature between the values of  $K_A$  for veronal at  $\mu = 0$ , namely  $3.7 \cdot 10^{-8}$  [9] and  $1.1 \cdot 10^{-8}$  [10], we measured the value ourselves at various temperatures by titrating a 0.1 M solution of the potassium salt of veronal with a 0.1 M solution of HCl at constant ionic strength  $\mu = 1.0$  (with KCl). The values of  $K_A$  obtained for veronal are given in Table 1. In the preceding paper [2], we took  $K_A$  for veronal equal to  $7.6 \cdot 10^{-8}$  ( $\mu = 1.0$ ) for purposes of calculation. In the present paper, the rate constants at  $25^\circ$  are referred to the value  $1.62 \cdot 10^{-8}$  ( $\mu = 1.0$ ) which we found for  $K_A$  of veronal.

Determination of rate constant. In all the buffer solutions studied, all the polarograms of maleic acid show that increasing the temperature increases both the absolute value of the kinetic current, and the ratio of the kinetic

current to the diffusion current, i.e.,  $i_{\text{kin}}/i_{\text{dif}}$ . The values of  $i_{\text{dif}}$  at different temperatures were found from the wave heights of the undissociated maleic acid in the acid solutions, with the introduction, following Ganush and Brdichka [11] of the correction factor 0.837, the same for all temperatures, which takes account of the difference between the diffusion coefficients of the acid and its di-anion. The values of the ratio of the diffusion current to the maleic acid concentration,  $i_{\text{dif}}/C$  (with the correction factor), are as follows: 15°, 2.28  $\mu\text{A}/\text{mM}$ ; 25°, 2.79  $\mu\text{A}/\text{mM}$ ; 35°, 3.16  $\mu\text{A}/\text{mM}$ ; and 45°, 3.51  $\mu\text{A}/\text{mM}$ .

To calculate  $\rho$ , the overall rate constant for the reaction of the maleic acid di-anion with the acids of the solution, i.e., the proton donors, the approximate Koutecký equation [3] could be used, derived for the saturation currents limited by the preceding chemical reaction

$$i_{\text{KIN}} = i_{\text{DIF}} \frac{0,886 \sqrt{\frac{\rho t}{\sigma}}}{1 + 0,886 \sqrt{\frac{\rho t}{\sigma}}}, \quad (1)$$

where  $\sigma$  is the equilibrium constant between the electrochemically inactive and the active form of the depolarizer [3]. In the present case,  $\sigma$  is the ratio of the concentrations of di-anion and mono-anion of maleic acid, i.e.,

$$\sigma = [A^{2-}]/[A^-]$$

The value of  $\sigma$  is determined by the second dissociation constant of maleic acid ( $K''_{\text{MA}}$ ) and the pH of the solution, and is independent of the composition and concentration of the components of the buffer system, so that

$$\sigma = K''_{\text{MA}}/[H^+]$$

A more exact solution of the depolarization problem with a preceding chemical reaction has been given by Koutecký, [3], in the form of a function  $\bar{F}(\chi_1) = i_{\text{kin}}/i_{\text{dif}}$ , expressing the ratio of the kinetic current to the diffusion current, where

$$\chi_1 = \sqrt{\frac{12 \rho t}{7 \sigma}} \quad (2)$$

Tables of the function  $\bar{F}(\chi_1)$  are given in the paper by Weber and Koutecký [12] which we used to calculate  $\rho$ .

However, neither of the solutions takes account of the effect of the spherical symmetry of the diffusion with respect to the mercury drop electrode. In a later paper, Koutecký and Cizek [13] took account of the spherical symmetry of the diffusion and gave a method of calculation, which consists in adding a small correction term to the function  $\bar{F}(\chi_1)$ , designated as  $\xi \bar{H}_C(\chi_1)$  [13].

The sequence of calculation of  $\rho$  in the present work was as follows. From the experimental values of  $i_{\text{kin}}/i_{\text{dif}} = \bar{F}(\chi_1)$ , using the tables of Ref. [12], (for convenience of interpolation between the tabular data, a curve was constructed) the approximate values of  $\chi_1$  were found, which were used to determine the spherical diffusion correction  $\xi \bar{H}_C(\chi_1)$  of Ref. [13], while  $\bar{H}_C(\chi_1)$  was found from the table of Ref. [13], and value of  $\xi$  was found from equating (45) of Ref. [13], as follows:

$$\xi = 50,4 D_2^{1/2} m^{-1/3} t^{1/6}, \quad (3)$$

where  $D_2$  is the diffusion coefficient of the maleic acid di-anion. In our case  $\xi$  was equal to 0.067 at 15°, 0.080 at 25°, 0.008 at 35°, and 0.0965 at 45°. From the corrected value of  $\bar{F}(\chi_1) = i_{\text{kin}}/i_{\text{dif}} + \xi \bar{H}_C(\chi_1)$  the table of Ref. [12], was used to find the value of  $\chi_1$ , and further  $\rho$  was calculated from equation (2).

The concentration of acids in the solution was calculated from the total concentration of the buffer system and the dissociation constant of its acid component. For this purpose it was necessary to know the values of the dissociation constants of the acids. The values of  $K'_a$  for boric acid in a KCl solution with  $\mu = 1$  at different temperatures are unknown. The only data in the literature are for  $K'_a$  in the solution of sodium salts. Since the values of  $K_a$  for acetic acid in salts of  $K^+$  and  $Na^+$  are close to one another, [14], we took for calculational purposes the values of  $K'_a$  for boric acid in NaCl solution ( $\mu = 1.0$ ) [14]. Their values are given in Table 1. To calculate the concentration of

TABLE 1. Rate Constants for the Reaction of the Maleic Acid Di-Anion with Proton Donor Acids at Various Temperatures

Acid	p	q	15°		25°		35°		45°	
			$K_A$	$k_A$ , liter/M·sec	$K_A$	$k_A$ , liter/M·sec	$K_A$	$k_A$ , liter/M·sec	$K_A$	$k_A$ , liter/M·sec
$NH_4^+$	1	1	$2.72 \cdot 10^{-10}$	$8.4 \cdot 10^2$ $1.4 \cdot 10^3$ $1.6 \cdot 10^3$	$5.59 \cdot 10^{-10}$	$2.8 \cdot 10^3$ $2.8 \cdot 10^1$ $2.2 \cdot 10^3$ $2.8 \cdot 10^3$ $2.8 \cdot 10^3$ $9.7$	$1.13 \cdot 10^{-9}$	$4.4 \cdot 10^3$ $4.4 \cdot 10^3$ $4.5 \cdot 10^3$	$2.14 \cdot 10^{-9}$	$1.0 \cdot 10^4$ $1.0 \cdot 10^4$ $1.2 \cdot 10^4$
	3	1	$1.28 \cdot 10^{-9}$	$5.3 \cdot 10^3$ $3.0 \cdot 10^3$ $3.6 \cdot 10^3$ $2.4 \cdot 10^3$ $2.0 \cdot 10^3$ $1.8 \cdot 10^3$	$1.57 \cdot 10^{-9}$	$8.28$ $8.68$ $8.68$ $9.08$ $9.08$ —	—	$8.12$ $6.0 \cdot 10^3$ $5.5 \cdot 10^3$ $5.5 \cdot 10^1$ $4.1 \cdot 10^3$ $3.0 \cdot 10^3$	—	$1.5 \cdot 10^4$ $9.3 \cdot 10^3$ $9.0 \cdot 10^3$ $9.2 \cdot 10^3$ $6.6 \cdot 10^3$ $3.9 \cdot 10^3$
	2	3	$3.32 \cdot 10^{-7}$	$5.0 \cdot 10^2$ $3.1 \cdot 10^2$ $3.0 \cdot 10^2$	$4.09 \cdot 10^{-12}$	$3.4 \cdot 10^2$ $1.4 \cdot 10^2$	$4.09 \cdot 10^{-12}$	$1.6 \cdot 10^2$ $3.0 \cdot 10^2$ $3.2 \cdot 10^2$	$4.09 \cdot 10^{-12}$	$3.0 \cdot 10^2$ $4.0 \cdot 10^2$
$H_3BO_3$	1	4	$4.09 \cdot 10^{-12}$	—	—	—	—	—	—	—
	2	1	$1.26 \cdot 10^{-8}$	$3.9 \cdot 10^4$ $2.8 \cdot 10^4$	$1.62 \cdot 10^{-8}$	$1.3 \cdot 10^5$ $1.1 \cdot 10^5$ $7.8 \cdot 10^4$ $5.6 \cdot 10^4$ $2.4 \cdot 10^{11}$ $1.6 \cdot 10^{-2}$	$2.46 \cdot 10^{-8}$	$2.0 \cdot 10^5$ $1.3 \cdot 10^5$	$3.31 \cdot 10^{-8}$	$3.5 \cdot 10^5$ $2.0 \cdot 10^5$
	1	1	$55.55$ $4.87 \cdot 10^{-17}$	$2.1 \cdot 10^{-11}$ $1.0 \cdot 10^{-2}$	$55.67$ $1.06 \cdot 10^{-16}$	—	$55.84$ $2.19 \cdot 10^{-16}$	$2.5 \cdot 10^{-11}$ $3.2 \cdot 10^{-2}$	$56.05$ $4.08 \cdot 10^{-16}$	$2.6 \cdot 10^{11}$ $5.0 \cdot 10^{-2}$
$H_2O^+$ $H_2O$	1	1	—	—	—	—	—	—	—	—
	1	1	—	—	—	—	—	—	—	—
	1	1	—	—	—	—	—	—	—	—

ammonium ions we used a value of  $K_a$  for ammonia, calculated from the  $K_b$  for  $\text{NH}_4\text{OH}$  and the  $K_w$  for water at different temperatures and an ionic strength equal to 1.0. To find the dissociation constant of phosphoric acid at different temperatures and ionic strength  $\mu = 1.0$ , we extrapolated the data of Table 1 and Fig. 1 from Ref. [15] to  $\mu = 1.0$ . Thus, we obtained values of  $K''$  (for  $\text{H}_2\text{PO}_4^-$ ) at  $\mu = 1.0$  for the temperatures 18, 25 and 37°, from which, taking account of the nature of the change of  $\text{p}K''$  for phosphoric acid with temperature [15,16], the value of  $K''$  for phosphoric acid was found graphically for the temperatures which we used. It must be noted, that  $K''$  for phosphoric acid was found graphically for the temperatures which we used. It must be noted, that  $K''$  reaches a maximum value at a temperatures 30-40°, consequently its value changes only slightly over the range of temperatures which we used. The values of the dissociation constant of phosphoric acid used for calculation are given in Table 1.

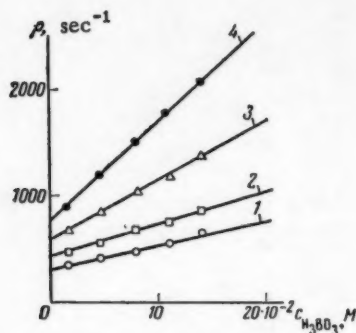


Fig. 1.  $\rho$  as a function of the concentration of undissociated boric acid at various temperatures: 1) 15° (pH 9.08); 2) 25° (pH 9.0); 3) 35° (pH 8.92); 4) 45° (pH 8.84).

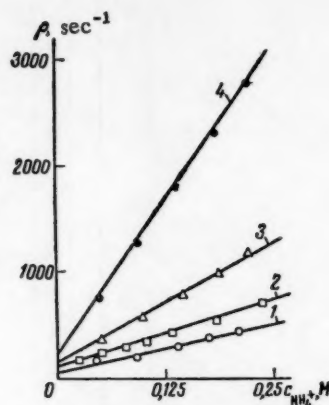


Fig. 2.  $\rho$  as a function of the concentration of ammonium ion: 1) 15° (pH 10.08); 2) 25° (pH 9.7); 3) 35° (pH 9.45); 4) 45° (pH 9.17).

In all the buffer systems which we studied at constant pH, the values vary linearly with the concentration of the acid components. As an example, Figs. 1 and 2 give data for one of the borate and one of the ammonium buffer solutions, taken at different temperatures. The values of  $\rho$  are the sum of the rate constants for the recombination reactions with all the proton donors in the solution, i.e.,

$$\rho = k_1[A_1] + k_2[A_2] + \dots + k_A[A],$$

where  $k_a$  is the rate constant for the reaction of the maleic acid di-anion with acid A, so that the slope of the straight lines giving  $\rho$  as a function of the concentration of one of the acid components, corresponds with the value of the particular rate constant  $K$  for the acid in question. The values of  $k_a$  found in this way are given in Table 1.

In phosphate solutions at the values of pH which we used, in addition to the hydrogen ions there are the two proton donors  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ , therefore, from the graph as a function of  $([\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}])$  only the total rate constant may be determined, thus:

$$k = k_{\text{H}_2\text{PO}_4^-}[\text{H}_2\text{PO}_4^-] + k_{\text{HPO}_4^{2-}}[\text{HPO}_4^{2-}].$$

If we represent the values of  $k/[\text{HPO}_4^{2-}]$ , obtained at different pH, in the form of a function of  $[\text{H}_2\text{PO}_4^-]/[\text{HPO}_4^{2-}]$ , the slope of the resulting straight lines may be used to determine  $k_{\text{H}_2\text{PO}_4^-}$  and then  $k_{\text{HPO}_4^{2-}}$ . Fig. 3 gives the straight lines of  $k/[\text{HPO}_4^{2-}]$  against  $[\text{H}_2\text{PO}_4^-]/[\text{HPO}_4^{2-}]$  for different temperatures. It should be noted that in the preceding paper [2], in calculating  $k$  for boric acid, the concentration of tetraboric acid was taken, by mistake, instead of the concentration of  $\text{H}_3\text{BO}_3$ ; therefore the value of  $k$  for boric acid given in [2] was too high.

The intercepts of the straight lines with the ordinate axis are the concentrations of acid corresponding with  $k_0$ , the total rate constant for the reaction of maleic acid di-anion with water and hydrogen ions.  $k_0$  is equal to  $k_{\text{H}_2\text{O}} \cdot [\text{H}_2\text{O}] + k_{\text{H}^+}[\text{H}^+]$ . Plotting  $\rho_0$  as a function of  $[\text{H}^+]$  makes it possible to determine  $k_{\text{H}^+}$ . As an example Figs. 4a and



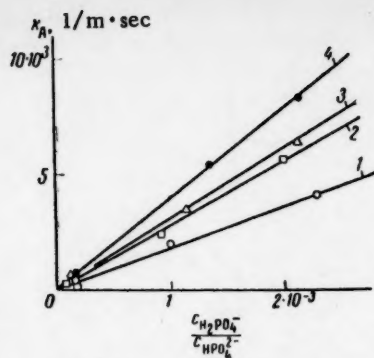


Fig. 3. Total rate constants with phosphate ions as a function of the ratio  $[H_2PO_4^-]/[HPO_4^{2-}]$  at various temperatures: 1) 15°; 2) 25°; 3) 35°; 4) 45°.

ponents of the buffer, account was taken of the change in  $pH_A$  of the acids from the secondary salt effect. These experiments showed principally the primary salt effect, which was especially marked in the work with phosphate solutions.

b give the values of  $\rho_0$  at 25 and 45°. The value of  $k_{H^+}$  was found by the method of least squares from the expression

$$\rho_0 = k_{H^+} [H^+],$$

i.e., without taking account of the rate constant for the reaction of the maleic acid di-anion with water, the value of which,  $k_{H_2O} [H_2O]$  at  $pH \leq 10$  is considerably less than  $k_{H^+} [H^+]$ . The values of  $k_{H^+}$  are given in Table 1. The value of  $k_{H^+}$  at 25°, found in the present work from a large amount of experimental data than in Ref. [2], seemed to be somewhat less than the value given in Ref. [2].

It must be noted, that at an ionic strength of  $\mu = 1.0$  in the solution, the electric double layer has practically no effect on the reaction being studied. We have verified this by special experiments, in which we studied the effect of KCl concentration on the protonation rate of maleic acid di-anions determined from the polarographic data. In making the experiments the pH of the solutions and the concentration of the buffer system were kept constant, and in calculating the concentration of the acid compo-

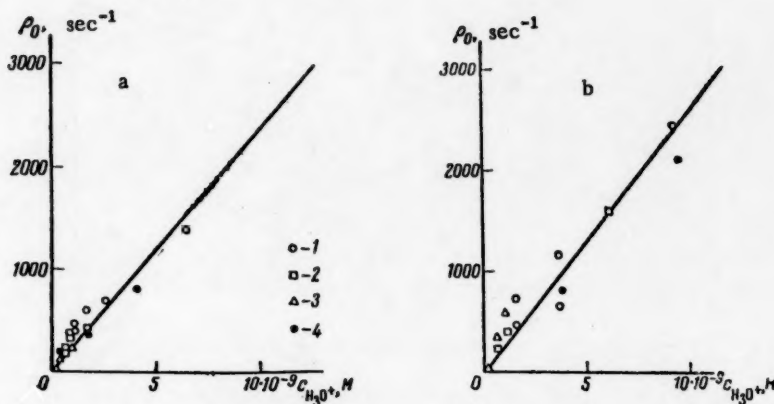


Fig. 4.  $\rho_0$  (value of  $\rho$  extrapolated to zero concentration of proton donors) as a function of hydrogen ion concentration in various buffer solutions: 1) borate, 2) ammonium, 3) phosphate, 4) veronal; a) for 25°, b) for 45°.

All the rate constants given in the present paper refer to solutions with ionic strength  $\mu = 1.0$ , the only cation (not counting  $H_3O^+$ ) outside of the ammonium solutions being  $K^+$ .

The experimentally determined values of  $k_A$  at all temperatures depend on the acid-proton donor constants  $K_A$  as given by Bronsted's equation [17]:

$$k_A = pG_1 \left( \frac{q}{p} K_A \right)^\alpha,$$

where  $\alpha < 1$  and  $G_1$  is a constant,  $p$  and  $q$  are the so-called statistical factors, which, respectively, take account of the number of protons which can be split off from the acid, and the number of places in the base to which the protons can be united. The values of  $p$  and  $q$  [17] are given in Table 1.

As an example, Fig. 5, a and b (the straight lines A) give graphs of Bronsted's equations for 15 and 45°. The

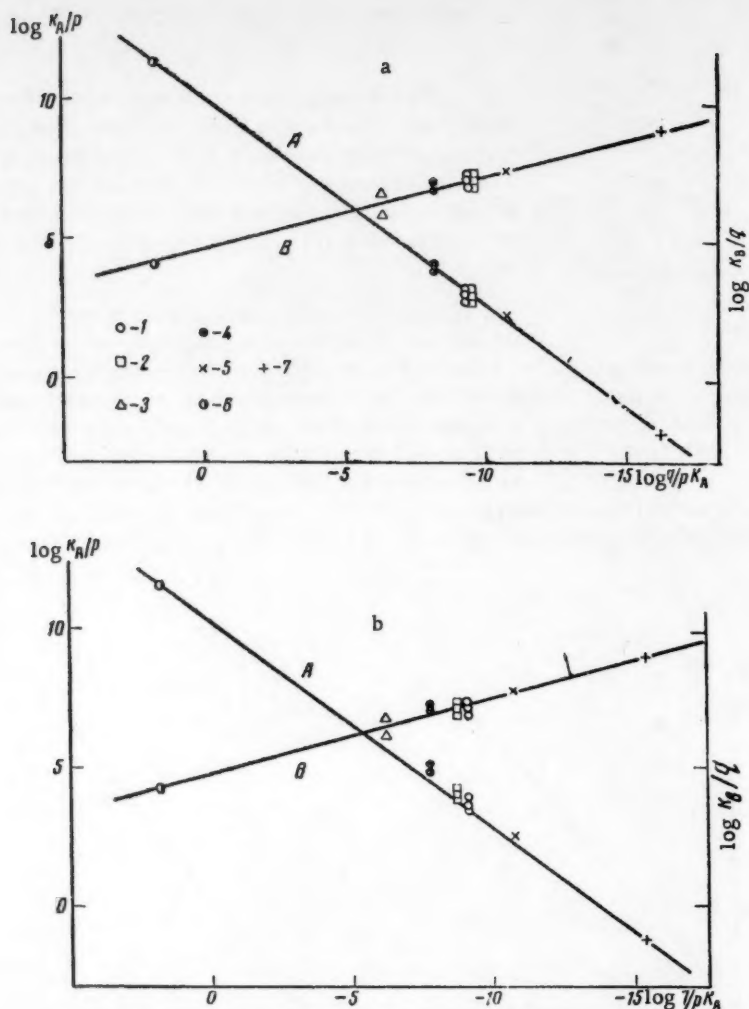


Fig. 5. Rate constants as a function of dissociation constants of acids and bases (from Bronsted's equation). The designations 1, 2, 4 are the same as in Fig. 4, 3)  $\text{H}_2\text{PO}_4^-$  ions, 5)  $\text{HPO}_4^{2-}$  ions, 6) hydroxonium ions, 7) water; a) for 15°, b) for 45°.

constants of Bronsted's equation for protonation of the maleic acid di-anions are, within the limits of experimental error, identical over the range of temperature studied:  $\alpha = 0.75$ ,  $\log G_1 = 10.2$ . The constancy of these quantities is due to the fact that the large increase in the rate constants with temperature for the weaker acids (corresponding with the right side of Fig. 5, a and b) is compensated for by the larger increase in their dissociation constants (compare the values of  $k_A$  and  $K_A$  at different temperatures in Table 1.) Extrapolating the straight lines representing Bronsted's equation, as in Ref. [2], gave the values of  $k_{\text{H}_2\text{O}}$ , given in Table 1. The extrapolation was made up to values of  $\log K_{\text{H}_2\text{O}}$  ( $\mu = 1.0$ ) for the temperatures in question. In Fig. 5, a and b, the values of  $k_{\text{H}_2\text{O}}$  found in this way are shown on the straight lines by crosses. The values of  $K_{\text{H}_2\text{O}}$  are likewise given in Table 1. These values were calculated from the values of  $K_W$  at different temperatures [14] using the values of  $\gamma_{\text{H}^+}\gamma_{\text{OH}^-}/a_{\text{H}_2\text{O}}$  in 1 N KCl [14].

The rate constants of the reverse reactions, the reaction of the maleic acid mono-anion with the corresponding bases, were calculated in the same way as in [2], starting with the rate constants of the di-anion recombination reaction and the acid dissociation constants. The values of the constants found in this way at 15 and 45° are given in Fig. 5, a and b on the straight lines B.

It should be noted that the highest value of  $k_{H^+}$  for the reaction between maleic acid di-anions and hydrogen ions is close to the highest theoretically possible value, which is equal, according to Debye [18] and Onsager [19], to the rate constant of the diffusion limited reaction between the hydrogen ion and the anion in solution.

**Energy and Entropy of Activation.** Figs. 6 and 7 give the values of the rate constant for the reaction of maleic acid di-anions with different proton donors in the form of a function of  $1/T$ . As can be seen from Figs. 6 and 7 the spread of the points is very large. The straight lines, corresponding with Arrhenius' equation, are constructed from values calculated by the method of least squares. An especially large spread in the rate constant values was observed for the reaction with the doubly charged anion  $HPO_4^{2-}$ , as it was not possible to determine the activation energy of this reaction from the data obtained. The experimental activation energies found from Figs. 6 and 7, the exponents,  $A$ , in Arrhenius' equation, and the values of activation entropy calculated from them [20] are given in Table 2. The table also gives the mean values of the rate constants for the di-anion reaction with various acids at  $25^\circ$ . As may be seen from Table 2, the activation energies of the reactions studied are rather low.

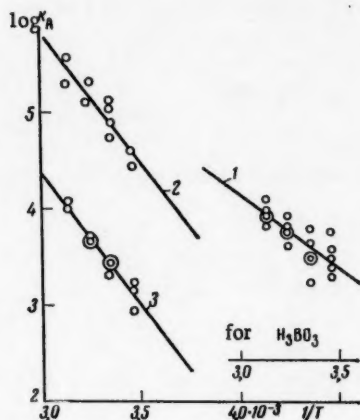


Fig. 6.  $\log k_A$  as a function of  $1/T$ : 1) for boric acid, 2) for the undissociated form of veronal, 3) for the ammonium ion.

TABLE 2

Acid	$k_A$ mean ( $25^\circ$ ), $1/M \cdot \text{sec}$	$E$ , $\text{kcal/M}$	$A$	$\Delta S^\ddagger$
$H_3O^+$	$2.2 \cdot 10^{11}$	2.1	$6.6 \cdot 10^{12}$	-1.6
$NH_4^+$	$2.6 \cdot 10^3$	12.4	$3.2 \cdot 10^{12}$	-3
$H_3BO_3$	$4.0 \cdot 10^3$	7.1	$6.3 \cdot 10^8$	-20
Veronal (undisso- ciated form)	$8.0 \cdot 10^4$	12.0	$3.2 \cdot 10^{13}$	3
$H_2O$	$1.6 \cdot 10^{-2}$	9.2	$6.9 \cdot 10^4$	-37
$H_2PO_4^-$	$2.5 \cdot 10^6$	4.3	$3.2 \cdot 10^9$	-17

The authors are grateful to M.G. Gonikberg for valuable discussions.

#### SUMMARY

1. A polarographic method was used at various temperatures to find the rate constants of the reaction between maleic acid di-anions and various proton donors, such as: hydrogen ions, boric acid, veronal, ammonium ions, mono- and di-anions of phosphoric acid, and water.

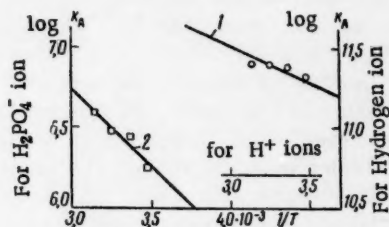


Fig. 7.  $\log k_A$  as a function of  $1/T$ : 1) for the hydrogen ion, 2) for the  $H_2PO_4^-$  ion.

It is well known that small values of experimental activation energy are characteristic of processes which are limited by the diffusion rate [20], where  $E$  is generally of the order of 4-5 kilo-cal, while for hydrogen ions this value is even lower [20]. The very small value of experimental activation energy observed in the reaction of maleic acid di-anions with hydrogen ions,  $\sim 2$  kilo-cal, once again confirms the diffusional nature of the limit on the right of this reaction. This is also shown by the nearly zero value of the activation entropy [20].

There is some interest in comparing the change in the exponent with the change in value of the product of the charges on the reacting particles,  $Z_{\text{di-anion}} \cdot Z_{\text{proton donor}}$ . As this product increases, the value of the exponent drops, in qualitative agreement with the theory of Ref. [20], (see the first three columns of Table 2). It must be kept in mind, that because of the large spread in the rate constants, the accuracy of the values for  $E$  and  $A$  is not very high, so that only qualitative conclusions may be drawn from them.

2. The values of the activation energy and the exponents in the Arrhenius' equation were found for the reactions studied.

3. The reaction of maleic acid di-anions with hydroxonium ions is determined only by the rate of the diffusion limited interaction between these ions.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# THE INDUCTIVE EFFECT IN THE OSCILLATIONAL FREQUENCIES OF THE BONDS Ge-H AND Ge-D

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We have already reported in Ref. [1] that a simple empirical relation exists between the inductive effect of substituents bound to silicon and germanium, and the oscillational frequencies of the bonds Si-H and Si-D, Ge-H and Ge-D. This relation is:

$$\nu = AX = A\Sigma x_R, \quad (1)$$

where  $\nu$  is the frequency of valence oscillation of the bond Si-H or Si-D, Ge-H or Ge-D,  $A$  is a constant quantity, equal to  $\sim 1011$  for hydrides and  $\sim 734$  for deuterides,  $X$  is the "effective" electronegativity of the silyl or germyl group, composed of the inductive constants ( $x_R$ ) of the three substituents bound with the silicon or the germanium. This relation results from the transformation of the Wilmshurst relation [2], based on the infinitesimally small effect which the mass of the substituents bound with silicon or germanium has on the frequency of oscillation of the Si-H and Si-D, Ge-H and Ge-D bonds. The problem of the present work was to refine this relation for hydrides and deuterides of germanium, for the purpose of finding a measure of the inductive effect of the substituents in the number of organic compounds of germanium and silicon. To this end, 21 hydrides and deuterides of germanium were prepared and their combined scattering spectra were taken (Table 1). The data obtained make it possible to express relation (1) for germanium deuterides in the following refined form:

$$\nu_{\text{Ge-D}} = 728 \cdot X_{\text{Ge}} = 728 \Sigma x_{\text{GeR}}, \quad (2)$$

where  $X_{\text{Ge}}$  is the "effective" electronegativity of the germyl group, and  $x_{\text{GeR}}$  gives the inductive constants of the substituents bound with the germanium. The value of  $A$  is equal to 1011 for both germanium hydrides and silicon hydrides.

The "effective" electronegativities of the germyl groups may be found from equations (1) or (2), from which it is easy to find the mean value of the "effective" inductive constants  $x_{\text{GeR}}$ . The mean inductive constants ( $x_{\text{GeR}}$ ) for a number of substituents have the following values:  $\text{C}_2\text{H}_5 - 0.664$ ,  $\text{CH}_2 = \text{CHCH}_2 - 0.664^*$ ,  $\text{C}_3\text{H}_7 - 0.667$ ,  $\text{CH}_3 - 0.670$ ,  $\text{CF}_3\text{CH}_2\text{CH}_2 - 0.680$ ,  $\text{H(D)} - 0.688$ ,  $\text{Br}^* - 0.698$ ,  $\text{Cl} - 0.712$ .

As is shown by the data of Table 1, the CSS frequencies  $\nu_{\text{Ge-H}}$  and  $\nu_{\text{Ge-D}}$ , calculated from Eqs. (1) and (2) are in satisfactory agreement with the experimental CSS frequencies. The values of the inductive constants of the substituents bound to the germanium were, as might be expected, proportional to the values of the inductive constants ( $x_{\text{SR}}$ ) of these same substituents, found from the "effective" electronegativities of the corresponding silyl groups. Fig. 1 speaks convincingly for this. Considering the natural spread in the values of the experimental frequencies for germanium hydrides and deuterides, as well as the somewhat lower ( $\pm 3 \text{ cm}^{-1}$ ) accuracy with which they are measured, compared with the frequencies of the silicon hydrides, it must be concluded that the proportionality shown is satisfactory. It is to be assumed that increasing the accuracy of frequency measurement and enlarging the range of compounds studied will make it possible to improve somewhat on the values for the inductive constants  $x_{\text{GeR}}$  given above. Comparison of the inductive constants  $x_{\text{GeR}}$  and  $x_{\text{SiR}}$  with the Taft polarity constants ( $\sigma^*$ ) also makes it possible to find an interesting relationship, which may be expressed for a number of simple trisubstituted silanes in the following

\* Required refinement.

\*\* Especially for  $\text{CH}_2 = \text{CHCH}_2\text{GeH}_3$ ,  $\text{CH}_2 = \text{CHCH}_2\text{GeD}_3$  and  $\text{Br}_3\text{GeH}$ .

TABLE 1

Formula of hydride (deuteride)	$\chi_{\text{Ge}} = \Sigma \chi_R$	$\nu_{\text{Ge-H}} \text{ or } \nu_{\text{Ge-D}} \text{ cm}^{-1}$		$\Delta$	Literature references
		Calculated	Found		
$\text{Cl}_3\text{GeH}$	2,136	2159	2158	+1	Present paper
$\text{BrCl}_2\text{GeH}$	2,122	2145	2144	+1	Ref. [3]
$\text{Br}_2\text{ClGeH}$	2,108	2131	2135	-4	" [3]
$\text{Br}_3\text{GeH}$	2,094	2117	2116	+1	" [3]
$\text{F}_2\text{CCH}_2\text{CH}_2\text{GeH}_3$	2,056	2077	2079	-2	Present paper
$\text{CH}_3\text{GeH}_3$	2,046	2069	2069	0	" "
$\text{C}_2\text{H}_5\text{GeH}_3$	2,043	2065	2067	-2	" "
$\text{CH}_2=\text{CHCH}_2\text{GeH}_3$	2,040	2062	2069	-7	" "
$\text{C}_3\text{H}_7\text{GeH}_3$	2,040	2062	2065	-3	" "
$(\text{CH}_3)_2\text{GeH}_2$	2,028	2050	2055	-5	" "
$(\text{C}_2\text{H}_5)_2\text{GeH}_2$	2,016	2038	2032	+6	" "
$(\text{CH}_3)_3\text{GeH}$	2,010	2032	2032	0	" "
$(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{GeH}$	2,004	2026	2022	+4	" "
$(\text{C}_2\text{H}_5)_3\text{GeH}$	1,992	2014	2010	+4	" "
$\text{Cl}_3\text{GeD}$	2,136	1555	1558	-3	" "
$\text{CH}_3\text{GeD}_3$	2,046	1489	1490	-1	" "
$\text{C}_2\text{H}_5\text{GeD}_3$	2,043	1487	1486	+1	" "
$\text{CH}_2=\text{CHCH}_2\text{GeD}_3$	2,040	1485	1480	+5	" "
$\text{C}_3\text{H}_7\text{GeD}_3$	2,040	1485	1480	+5	" "
$(\text{CH}_3)_2\text{GeD}_2$	2,028	1476	1480	-4	" "
$(\text{C}_2\text{H}_5)_2\text{GeD}_2$	2,016	1468	1467	+1	" "
$(\text{CH}_3)_3\text{GeD}$	2,010	1463	1466	-3	" "
$(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{GeD}$	2,004	1459	1458	+1	" "
$(\text{C}_2\text{H}_5)_3\text{GeD}$	1,992	1450	1452	-2	" "

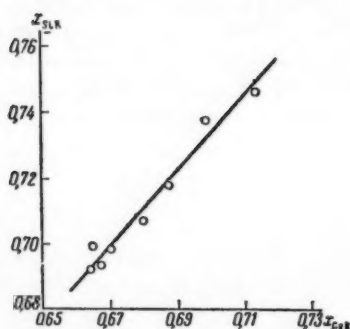


Fig. 1. Relation between the inductive constants ( $\chi_{\text{SiR}}$ ) and ( $\chi_{\text{GeR}}$ ), found from the values of the "effective" electronegativities of the corresponding silyl and germyl groups.

approximate form:

$$\Sigma \sigma^* = 57.8 \Sigma \chi_{\text{SiR}} - 120.34. \quad (3)$$

This relationship follows logically from Eq. (1) and the approximate equation proposed recently by Thompson in Ref. [4]. It is shown in Fig. 2.

The direct relationship between the inductive constants  $\chi_{\text{SiR}}$  and  $\chi_{\text{GeR}}$ , and the Taft polarity constants ( $\sigma^*$ ) gives some reason to expect that for some reactions of silicon and germanium organic compounds there will be a relationship between reactivity and structure, similar to the equations of Taft or Hammett\*

\* For silico-organic compounds a similar relation was first found by Hyde, Brown, and Smith [13] and quite recently by Steward and Pierce [14].

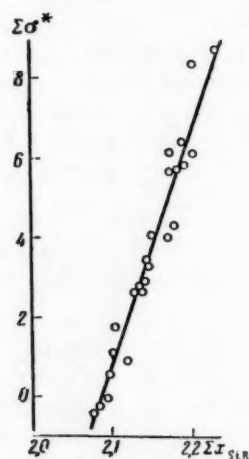


Fig. 2. Relation between the inductive constants ( $\chi_{\text{SiR}}$ ) and the Taft polarity constants ( $\sigma^*$ ) for a number of simple tri-substituted silanes.

TABLE 2

Alkyl germanium chloride	Quantity, g	Quantity of LiH and LiD	Solvent	Quantity, ml	Alkyl germanium hydride (deuterides)	Yield, g (%)	B.p., °C (p in mm Hg)	$d_4^{20}$	$n_D^{20}$	M/R	
										Found	Calc.
$\text{CH}_3\text{CH}_2\text{CH}_2\text{GeCl}_2$	66	16	Dioxane	100	$\text{C}_4\text{H}_9\text{GeH}_2$	20,0 (35,3)	41-42,5(757)	1,0391	1,4130	28,50	27,46
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{GeCl}_2$	66	12	"	150	$\text{C}_4\text{H}_9\text{GeD}_3$	10,5 (29)	41,5 (754)	1,0508	1,4055	28,42	27,40
$\text{CF}_3\text{CH}_2\text{CH}_2\text{GeCl}_2$	31	6	"	75	$\text{CF}_3\text{CH}_2\text{CH}_2\text{GeH}_2$	4,7 (25)	46(750,5)	1,3362	1,3530	28,02	27,55
$\text{CH}_2=\text{CHCH}_2\text{GeCl}_2$	30	6	"	75	$\text{C}_3\text{H}_7\text{GeH}_2$	4,5 (28)	37(752,7)	1,0797	1,4315	28,00	26,99
$\text{CH}_2=\text{CHCH}_2\text{GeCl}_2$	32,5	8	"	100	$\text{C}_3\text{H}_7\text{GeD}_2$	4,3 (24)	37(744)	1,1146	1,4320	27,87	26,93
$(\text{C}_4\text{H}_9)_3\text{GeCl}$	20	4	Diisoamyl ether	50	$(\text{C}_4\text{H}_9)_3\text{GeH}$	4,0 (24)	120(750,5)	1,0043	1,4338	41,69	41,61
$(\text{C}_4\text{H}_9)_3\text{GeCl}$	14,7	6	"	50	$(\text{C}_4\text{H}_9)_3\text{GeD}$	3,8 (31)	120(740)	1,0097	1,4333	41,67	41,49

TABLE 3

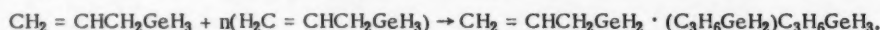
Unsaturated compound	Quantity, g	Quantity, g	Quantity of $\text{HGeCl}_3$ + $\text{GeCl}_4$ , g	Combination product	Yield, g (%)	B.p., °C (p in mm Hg)	$d_4^{20}$	$n_D^{20}$	M/R	
									Found	Calc.
$\text{CH}_3\text{CH}=\text{CH}_2$	—	—	130	$\text{CH}_3\text{CH}_2\text{CH}_2\text{GeCl}_2$	55,7 (50)	160(749)	1,5006	1,4730	40,18	41,52
$\text{CF}_3\text{CH}=\text{CH}_2$	—	—	120	$\text{CF}_3\text{CH}_2\text{CH}_2\text{GeCl}_2$	52,7 (29)	143(758)	1,7105	1,4233	41,12	40,27
$\text{CF}_2=\text{CH}_2$	—	—	56	$\text{C}_2\text{F}_5\text{H}_2\text{GeCl}_2$	35,0 (47)	140(752)	1,7992	1,4480	33,61	36,37
$\text{ClFCHCF}_2\text{OCH}_2\text{CH}=\text{CH}_2$	73	73	81,5	$\text{ClFCHCF}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{GeCl}_2$	64,3 (44)	110-123(10)	1,6817	1,4523	56,14	56,00
$\text{CH}_2=\text{CHCH}_2\text{Br}$	62	62	90	$\text{CH}_2=\text{CHCH}_2\text{GeCl}_2$	30,0 (27)	154(745,5)	—	—	—	—

$$\lg k/k_0 = a(X_{\text{Ge}} - X_{\text{Ge}}^0) = a'(X_{\text{Si}} - X_{\text{Si}}^0). \quad (4)$$

The results of competitive combination of silicon hydrides with unsaturated compounds in the presence of platinized charcoal [5-7], the marked orientational effect of silyl and germyl groups in the radical and electrophilic halogenation of alkyl- and aryl silane (germane) chlorides and fluorides [8-10] and a number of other data [11] may be considered to be qualitative experimental justification for the existence of Eq. (4). The limits of application of Eq. (1), as well as the amount of reality to be attached to Eq. (4), will, obviously, be determined by the importance of other than inductive effects, such as, steric effect, coordinational unsaturation of the central atom, intermolecular interaction, etc.

## EXPERIMENTAL

**Preparation of Alkyl Germanium Hydrides and Deuterides.** The organic hydrides and deuterides of germanium shown in Tables 1 and 2 were prepared from the corresponding chlorides, by reacting them with lithium hydride or deuteride in dioxane or diisoamyl ether, using the technique described previously in Ref. [12]. The boiling point, the specific gravity, and the index of refraction of  $\text{CH}_3\text{GeH}_3$ ,  $(\text{CH}_3)_2\text{GeH}_2$ ,  $(\text{CH}_3)_3\text{GeH}$ ,  $\text{C}_2\text{H}_5\text{GeH}_3$ ,  $(\text{C}_2\text{H}_5)_2\text{GeH}_2$ ,  $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{GeH}$ ,  $\text{CH}_3\text{GeD}_3$ ,  $\text{C}_2\text{H}_5\text{GeD}_3$ ,  $(\text{CH}_3)_2\text{GeD}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{GeD}_2$ ,  $(\text{CH}_3)_3\text{GeD}$  and  $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{GeD}$  agreed with the values for the same products prepared by us in Ref. [12]. The properties and methods of preparation of the new hydrides and deuterides used in the present paper are given in Table 2. Interesting properties were shown by  $\text{CH}_2 = \text{CHCH}_2\text{GeH}_3$ . Under the influence of heat or simply on standing it polymerizes to form a solid polymer having the composition  $(\text{CH}_2\text{CH}_2\text{CH}_2\text{GeH}_2)_x$ . The reaction obviously proceeds according to the scheme



In this respect  $\text{CH}_2 = \text{CHCH}_2\text{GeH}_3$  suggests  $\text{CH}_2 = \text{CHGeH}_3$  [15], differing from  $\text{CH}_2 = \text{CHCH}_2\text{SiH}_3$ , which may be explained by the higher coordination unsaturation of germanium, and the lower strength and greater polarity of the  $\text{GeH}$  bond.  $\text{HGeCl}_3$  and  $\text{DGeCl}_3$  mixed with  $\text{GeCl}_4$  were prepared by passing  $\text{HCl}$  or  $\text{DCl}$  over finely divided germanium at 400-450°.

**Preparation of Alkyl Germanium Halides.**  $\text{CH}_3\text{GeCl}_3$ ,  $(\text{CH}_3)_2\text{GeCl}_2$ ,  $\text{C}_2\text{H}_5\text{GeCl}_3$  were prepared by a direct method under the conditions described previously in Ref. [16].  $(\text{C}_2\text{H}_5)_2\text{GeCl}_2$  and  $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{GeBr}$  were prepared by the method of Ref. [12] from  $\text{C}_2\text{H}_5\text{GeCl}_3$ ,  $(\text{CH}_3)_2\text{GeCl}_2$  and  $\text{C}_2\text{H}_5\text{MgBr}$ .  $\text{CH}_3\text{CH}_2\text{CH}_2\text{GeCl}_3$ ,  $\text{CF}_3\text{CH}_2\text{CH}_2\text{GeCl}_3$ ,  $\text{CF}_2\text{HCH}_2\text{GeCl}_3$ ,  $\text{CF}(\text{Cl})\text{HCF}_2\text{OCH}_2\text{CH}_2\text{GeCl}_3$  were prepared by combining  $\text{HGeCl}_3$  with the corresponding unsaturated compounds, using the method described in Ref. [17] (Table 3). Allyltrichlorogermane was prepared as in Ref. [18].

**Combined Scattering Spectra.** The CSS spectra of the hydrides and deuterides shown in Table 1 were taken on a three prism ISP-51 spectrograph using the mercury line 4358 Å for exhortation. The spectra of all the compounds were taken in the liquid phase, and the frequencies were measured with an accuracy of  $\pm 3 \text{ cm}^{-1}$ .

## SUMMARY

1. A refinement has been made on the imperical relation between the oscillational CSS frequencies of a number of hydrides and deuterides of germanium of the type  $\text{R}_3\text{GeH(D)}$  and the inductive effect of substituents R.
2. A connection has been found between the inductive constants of substituents in hydrides and deuterides of germanium and silicon, and Taft's polarity constants.
3. A number of organic hydrides and deuterides of germanium have been prepared and an enhanced tendency of allyl germanium compounds to polymerization has been demonstrated.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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# THE EFFECT OF THE THERMODYNAMIC ISOTOPE EFFECT ON THE DISTRIBUTION OF ISOTOPIC MOLECULES

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In 1937 Brodskii [1] gave a formula, not including isotope effects, for calculating the mole fractions of isotopic molecules  $AX_{n-1}X_i$  in the compound  $AX_n$ , one element of which, X, consists entirely of the two isotopes X and X\*. In 1957 Petrenko [2] indicated a general method of finding the mole fractions of different isotopic molecules of any compound (also neglecting isotope effects) and showed that the number (P) of different isotopic molecules of a compound (I): ( ${}^1E_{N_1} \dots {}^iE_{N_i} \dots {}^xE_{N_x}$ ), consisting of  $x$  different elements  ${}^1E, \dots, {}^iE, \dots, {}^xE$ , each of which consists of  $z_i$  isotopes, is equal to

$$\Pi = \prod_{i=1}^x \frac{(N_i + z_i - 1)!}{N_i! (z_i - 1)!}, \quad (1)$$

where  $N_i$  is the number of atoms of the  $i$ 'th element ( ${}^iE$ ) in the molecule, and  $z_i$  is the number of isotopes of the  $i$ 'th element.

In 1960 Nefedov et. al. [3] gave a more convenient formula than the one given in Ref. [2] for calculating the mole fraction of any of the isotopic compounds of compound (I) (likewise neglecting isotope effects)

$$n = \prod_{i=1}^x \frac{N_i!}{\alpha_1^i! \dots \alpha_k^i! \dots \alpha_{z_i}^i!} \cdot (a_1^i)^{\alpha_1^i} \dots (a_k^i)^{\alpha_k^i} \dots (a_{z_i}^i)^{\alpha_{z_i}^i}, \quad (2)$$

where  $n$  is the mole fraction of the isotopic compound

$$E_{N_1}^{\alpha_1^1(1) \dots \alpha_k^1(k) \dots \alpha_{z_1}^1(z_1)} \dots E_{N_i}^{\alpha_1^i(1) \dots \alpha_k^i(k) \dots \alpha_{z_i}^i(z_i)} \dots E_{N_x}^{\alpha_1^x(1) \dots \alpha_k^x(k) \dots \alpha_{z_x}^x(z_x)},$$

i.e., the compound the molecules of which contain  $\alpha_1^i$  atoms of the 1st isotope of the  $i$ 'th element,  $\dots, \alpha_k^i$  atoms of the  $k$ 'th isotope of the  $i$ 'th element,  $\dots$  and  $\alpha_{z_i}^i$  atoms of the  $z_i$ 'th isotope of the  $i$ 'th element [in what follows we shall designate this isotopic compound by the symbol (II)],  $\alpha_k^i$  is the atomic fraction of the  $k$ 'th isotope in the  $i$ 'th element, and  $N_i$  is the number of atoms of the  $i$ 'th element in the molecule.

Formula (2) gives the mole fractions of isotopic compounds of any compound, starting from purely statistical ideas, without considering the possible influence of isotope effects on the distribution of the isotopic molecules. Meanwhile it is clear, that in the case of isotopic molecules in thermodynamic equilibrium with one another (i.e., capable, under definite conditions, of engaging in isotope exchange with one another), the thermodynamic isotope effect (TIE) must cause the actual distribution of isotopic molecules to depart from the statistical value, given by formula (2). The TIE should be observable in the case of light elements and particularly in the case of hydrogen.

The purpose of the present paper is to determine how much effect TIE has on the distribution of isotopic molecules, and to indicate methods of calculating the mole fractions of isotopic molecules taking account of TIE. The whole assembly of isotopic molecules (II) of the compound (I), the number of which is equal to P, may be obtained from the  $\prod_{i=1}^x z_i$  of homoisotopic molecules (i.e., molecules, every element of which is represented by only one of its

isotopes) by equation (3)

$$\sum_{h_1=1}^{z_1} \dots \sum_{h_i=1}^{z_i} \dots \sum_{h_x=1}^{z_x} \alpha_{h_1}^1 \dots \alpha_{h_i}^i \dots \alpha_{h_x}^x (E_{N_1}^{N_1(h_1)} \dots E_{N_i}^{N_i(h_i)} \dots E_{N_x}^{N_x(h_x)}) \\ = N_1 \dots N_x \quad (\text{II}). \quad (3)$$

In its turn, the number  $\prod_{i=1}^x z_i - \sum_{i=1}^x (z_i - 1) - 1$  of homoisotopic molecules in the total number  $\prod_{i=1}^x z_i$  may be obtained from the  $1 + \sum_{i=1}^x (z_i - 1)$  of the other homoisotopic molecules by Eq. (4)

$$\sum_{i=1}^x (E_{N_1}^{N_1(1)} \dots E_{N_{i-1}}^{N_{i-1}(1)} E_{N_i}^{N_i(h_i)} E_{N_{i+1}}^{N_{i+1}(1)} \dots E_{N_x}^{N_x(1)}) = \\ (x-1) (E_{N_1}^{N_1(1)} \dots E_{N_x}^{N_x(1)}) + (E_{N_1}^{N_1(h_1)} \dots E_{N_i}^{N_i(h_i)} \dots E_{N_x}^{N_x(h_x)}). \quad (4)$$

Eqs. (3) and (4) represent nothing other than the general formula for the isotope exchange between  $1 + \sum_{i=1}^x (z_i - 1)$  homoisotopic molecules, which causes the formation of the isotopic molecule (II), and they have the following equilibrium constants respectively

$$K = \frac{\alpha_1^1 \dots \alpha_{h_i}^i \dots \alpha_{z_i}^i}{\alpha_1^x \dots \alpha_{h_i}^x \dots \alpha_{z_x}^x} \\ = \frac{[(\text{II})]^{N_1 \dots N_x}}{\prod_{h_x=1}^{z_x} \dots \prod_{h_i=1}^{z_i} \dots \prod_{h_1=1}^{z_1} [(E_{N_1}^{N_1(h_1)} \dots E_{N_i}^{N_i(h_i)} \dots E_{N_x}^{N_x(h_x)})]^{a_{h_1}^1 \dots a_{h_i}^i \dots a_{h_x}^x}} \quad (5)$$

$$K \begin{vmatrix} N_1(h_1) \\ \dots \\ N_i(h_i) \\ \dots \\ N_x(h_x) \end{vmatrix} = \frac{[(E_{N_1}^{N_1(1)} \dots E_{N_x}^{N_x(1)})]^{x-1} [(E_{N_i}^{N_i(h_i)} \dots E_{N_1}^{N_1(h_1)} \dots E_{N_x}^{N_x(h_x)})]}{\prod_{i=1}^x [(E_{N_1}^{N_1(1)} \dots E_{N_{i-1}}^{N_{i-1}(1)} E_{N_i}^{N_i(h_i)} E_{N_{i+1}}^{N_{i+1}(1)} \dots E_{N_x}^{N_x(1)})]} \quad (6)$$

Altogether, for compound (I),  $P$  equilibrium constants may be found, however,  $1 + \sum_{i=1}^x (z_i - 1)$  of them are found to be not independent and may be expressed in terms of the constants (5) and (6). The total number of independent constants (5) and (6) is equal to  $P - \prod_{i=1}^x z_i$  and  $\prod_{i=1}^x z_i - \sum_{i=1}^x (z_i - 1) - 1$ , respectively. These equilibrium constants may either be calculated theoretically from statistical thermodynamics or they may be determined experimentally.

Let the  $k$ 'th isotope ( ${}^k\text{E}$ ) have an atomic fraction of  $i$ 'th element ( ${}^i\text{E}$ ) equal to  $a_{ik}^i$ . The material balance equation of this isotope is given by formula (7)

$$\sum_{\alpha_h=1}^{N_i} \frac{\alpha_h^i}{N_i} [(\Pi)] = a_h^i. \quad (7)$$

To find the distribution of isotopic molecules (II) in the compound (I), the number of which is equal to P we must set up a system of P equations. For this purpose take  $\Pi - \prod_{i=1}^x z_i$  equations from (5),  $\prod_{i=1}^x z_i - \sum_{i=1}^x (z_i - 1) - 1$  equations from (6),  $\sum_{i=1}^x (z_i - 1)$  equations from (7), set up for the  $(z_i - 1)$  isotopes of each element ( ${}^iE$ ), and one equation, expressing the material balance of the system

$$\sum_{\alpha_1^1=0}^{N_1} \dots \sum_{\alpha_{z_1-1}^1=0}^{N_1 - \sum_{s=1}^{z_1-2} \alpha_s^1} \dots \sum_{\alpha_1^i=0}^{N_i} \sum_{\alpha_2^i=0}^{N_i - \alpha_1^i} \dots \sum_{\alpha_k^i=0}^{N_i - \sum_{s=1}^{k-1} \alpha_s^i} \dots \sum_{\alpha_{z_i-1}^i=0}^{N_i - \sum_{s=1}^{z_i-2} \alpha_s^i} \dots \sum_{\alpha_1^x=0}^{N_x} \dots \sum_{\alpha_{z_x-1}^x=0}^{N_x - \sum_{s=1}^{z_x-2} \alpha_s^x} \dots \sum_{\alpha_{z_x-1}^x=0}^{N_x - \sum_{s=1}^{z_x-2} \alpha_s^x} [(II)] = 1. \quad (8)$$

Eq. (8) shows that the sum of the mole fractions of all the isotopic molecules is equal to 1.

The solution of the system of P equations gives the mole fractions of all P isotopic molecules. However, the solution of the P equations (5), (6), (7) and (8) in general form encounters insuperable mathematical difficulties. Therefore, the problem will be solved for only a few special cases. First of all we will consider the case where only one of the elements of compound (I) consists of different isotopes (the remaining elements are taken to be mono-isotopic). Then the compound (I) will be designated by the formula  $RE_N$ , where R is the rest of the molecule, which does not contain E atoms which are capable of isotope exchange. The isotopic molecule (I) will be designated thus:  $RE_N^{\alpha_1(1)...\alpha_k(k)...\alpha_z(z)}$ , i.e.,  $\alpha_1$  atoms of element E represent the isotope  $E^1$ , ...,  $\alpha_k$  atoms of element E represent isotope  $E^k$ , ..., and  $\alpha_z$  atoms of element E represent isotope  $E^z$ , ..., and  $\alpha_z$  atoms represent isotope  $E^z$  (thus the element E has z isotopes altogether), N is the number of atoms of element E, occurring in thermodynamic equilibrium.

We shall now consider some more special cases.

The Element E Consists of Two Isotopes ( $z = 2$ ),  $N$  Arbitrary,  $x = 1$ . According to formula (1), for the case  $x = 1$  and  $z = 2$ , the total number of isotopic molecules is  $P = N + 1$ . To find the mole fractions of these isotopic molecules we set up a system of equations from the  $N-1$  independent equilibrium constants-one material balance equation for one of the isotopes, and one material balance equation for the isotopic molecules (the number of equations (6) at  $x = 1$  is equal to 0):

[illegible]

$$\sum_{i=0}^N [\text{RE}_N^{i(1)N-i(2)}] = 1 \quad (9)$$

It may be shown that after substitution

$$[\text{RE}_N^{N(2)}] = \alpha [\text{RE}_N^{N(1)}] \quad (10)$$

and the solution of the system of equations (9) is a matter of solving N'th degree equation in  $\alpha^{1/N}$

$$\alpha + \left(1 - \frac{1}{Na_1}\right) K_{N-1}^{\frac{1}{N}} \alpha^{\frac{N-1}{N}} + \left(1 - \frac{2}{Na_1}\right) K_{N-2}^{\frac{2}{N}} \alpha^{\frac{N-2}{N}} + \left(1 - \frac{3}{Na_1}\right) K_{N-3}^{\frac{3}{N}} \alpha^{\frac{N-3}{N}} + \dots + \left(1 - \frac{N-1}{Na_1}\right) K_1^{\frac{1}{N}} \alpha^{\frac{1}{N}} + \left(1 - \frac{1}{a_1}\right) = 0. \quad (11)$$

Having found the value of  $\alpha$  from Eq. (11), the mole fraction  $[\text{RE}_N^{N(1)}]$  is found from Eq. (12)

$$[\text{RE}_N^{N(1)}] = \frac{a_1}{1 + \frac{N-1}{N} K_1^{\frac{1}{N}} \alpha^{\frac{1}{N}} + \frac{N-2}{N} K_2^{\frac{2}{N}} \alpha^{\frac{2}{N}} + \dots + \frac{2}{N} K_{N-2}^{\frac{N-2}{N}} \alpha^{\frac{N-2}{N}} + \frac{1}{N} K_{N-1}^{\frac{1}{N}} \alpha^{\frac{N-1}{N}}}. \quad (12)$$

Then using the value of  $[\text{RE}_N^{N(1)}]$  found from Eq. (10),  $[\text{RE}_N^{N(2)}]$  is found. Finding the mole fractions of the remaining isotopic molecules no longer presents any difficulties.

**Example 1.**  $N = 2$ ,  $z = 2$ ,  $a_1$  is the atomic fraction of isotope  $E^1$  and element E. In this case three isotopic molecules are possible altogether:  $\text{RE}_2^{2(1)}$ ,  $\text{RE}_2^{1(1)1(2)}$  and  $\text{RE}_2^{2(2)}$  and one equilibrium constant:  $K[\text{RE}_2^{2(1)}][\text{RE}_2^{2(2)}] = [\text{RE}_2^{1(1)1(2)}]^2$ . Eq. (11) takes the form:

$$\alpha + \left(1 - \frac{1}{2a_1}\right) K^{\frac{1}{2}} \alpha^{\frac{1}{2}} + \left(1 - \frac{1}{a_1}\right) = 0. \quad (13)$$

Solving Eq. (13) and substituting the value of  $\alpha$  obtained in Eq. (12) gives

$$[\text{RE}_2^{2(1)}] = \frac{K}{2(4-K)} + a_1 - \sqrt{\frac{K^2}{4(4-K)^2} + \frac{K}{4-K}} (a_1 - a_1^2); \quad (14)$$

$$[\text{RE}_2^{2(2)}] = \frac{K}{2(4-K)} + 1 - a_1 - \sqrt{\frac{K^2}{4(4-K)^2} + \frac{K}{4-K}} (a_1 - a_1^2); \quad (15)$$

$$[\text{RE}_2^{1(1)1(2)}] = -\frac{K}{4-K} + 2 \sqrt{\frac{K^2}{4(4-K)^2} + \frac{K}{4-K}} (a_1 - a_1^2). \quad (16)$$

It may be shown that the relative deviation of the mole fraction  $n^*$  of the isotopic molecule  $\text{RE}_2^{2(1)}$ , calculated from formula (14), from the mole fraction  $\underline{n}$ , calculated neglecting TIE as in formula (2), is increased with decreasing  $a_1$ , thus,

$$\lim_{a_1 \rightarrow 0} \frac{n^* - \underline{n}}{\underline{n}} = \frac{4}{K} - 1. \quad (17)$$

The quantity  $\left[\frac{4}{K} - 1\right]$  gives the deviation of the system in question from the ideal and is equal to the maximum possible effect of TIE on the composition of the isotopic molecule  $\text{RE}_2^{2(1)}$ . Formulas (14)-(16) may be reasonably used for not too low values of  $a_1$ . At  $a_1 < 0.01$ , sufficiently accurate results are given by formula (17).

Table 1 gives several examples of the effect of TIE on the distribution of isotopic molecules. The values of  $\underline{n}$

TABLE 1. Effect of TIE on the Distribution of Isotopic Molecules and Several Compounds

System	Isotopes	Value of K and Literature reference	Maximum TIE 4/K-1, %	Isotopic Molecules	n, % (a <sub>1</sub> =0.5)	n*, % (a <sub>1</sub> =0.5)	TIE at a <sub>1</sub> =0.5 $\frac{n^*-n}{n}$ , %
H <sub>2</sub>	H, D	3,28 [4] (at 298° K)	21,95	H <sub>2</sub>	25	26,24	+4,96
				HD	50	47,52	-4,96
				D <sub>2</sub>	25	26,24	+4,96
H <sub>2</sub>	H, T	2,85 [5] (at 298° K)	40,35	H <sub>2</sub>	25	27,1854	+8,74
				HT	50	45,6292	-8,74
				T <sub>2</sub>	25	27,1854	+8,74
N <sub>2</sub>	N <sup>14</sup> , N <sup>15</sup>	3,6 [6] (at 450° K)	11,11	N <sub>2</sub> <sup>2(14)</sup>	25	25,66	+2,64
				N <sub>2</sub> <sup>1(14)1(15)</sup>	50	48,64	-2,64
				N <sub>2</sub> <sup>2(15)</sup>	25	25,66	+2,64
CO <sub>2</sub>	C <sup>12</sup> , O <sup>16</sup> , O <sup>18</sup>	3,983 [6] (at 273,1°K)	0,48	C <sup>12</sup> O <sub>2</sub> <sup>2(16)</sup>	25	25,027	+0,108
				C <sup>12</sup> O <sub>2</sub> <sup>1(16)1(18)</sup>	50	49,946	-0,108
				C <sup>12</sup> O <sub>2</sub> <sup>2(18)</sup>	25	25,027	+0,108
N <sub>2</sub> O	O <sup>16</sup> , N <sup>14</sup> , N <sup>15</sup>	3,964 * [6] (at 273,1°K)	0,91	N <sup>14</sup> N <sup>14</sup> O	25	25,0655	+0,262
				N <sup>14</sup> N <sup>15</sup> O	50	49,869	-0,262
				N <sup>15</sup> N <sup>14</sup> O			
				N <sup>15</sup> N <sup>15</sup> O	25	25,0655	+0,262

\* It is assumed that the TIE for the molecule N14 N15 O and N15 N14 O is the same.

at  $a_1 = 0.5$  are calculated from formula (2), and the values of  $n^*$  are calculated from formulas (14)-(16).

**Example 2.**  $N = 3$ ,  $z = 2$ ,  $a_1$  is the atomic fraction of isotope  $E^1$  in element E. In this case four isotopic molecules are possible:  $RE_3^{3(1)}$ ,  $RE_3^{2(1)1(2)}$ ,  $RE_3^{1(1)2(2)}$ ,  $RE_3^{3(2)}$ , and two independent equilibrium constants for the isotope exchange:

$$K_1 = [RE_3^{2(1)1(2)}]^3 / [RE_3^{3(1)}]^2 [RE_3^{3(2)}] \text{ and } K_2 \\ = [RE_3^{1(1)2(2)}]^3 / [RE_3^{3(1)}] [RE_3^{3(2)}]^2.$$

Eqs. (11) and (12) take on the following forms respectively:

$$\alpha + \left(1 - \frac{1}{3a_1}\right) K_2^{\frac{1}{3}} \alpha^{\frac{2}{3}} + \left(1 - \frac{2}{3a_1}\right) K_1^{\frac{1}{3}} \alpha^{\frac{1}{3}} + \left(1 - \frac{1}{a_1}\right) = 0, \quad (18)$$

$$[RE_3^{3(1)}] = \frac{a_1}{1 + \frac{2}{3} K_1^{\frac{1}{3}} \alpha^{\frac{1}{3}} + \frac{1}{3} K_2^{\frac{1}{3}} \alpha^{\frac{2}{3}}} \quad (19)$$

The difference between the mole fraction  $[RE_3^{3(1)}]^*$ , calculated with TIE, and the mole fraction  $[RE_3^{3(1)}]$  calculated from Eq. (2) without TIE, increases with decreasing  $a_1$ , thus

$$\lim_{a_1 \rightarrow 0} \frac{[RE_3^{3(1)}]^* - [RE_3^{3(1)}]}{[RE_3^{3(1)}]} = \frac{27}{K_2} - 1, \quad (20)$$

$$\lim_{a_1 \rightarrow 0} \frac{[RE_3^{2(1)1(2)}]^* - [RE_3^{2(1)1(2)}]}{[RE_3^{2(1)1(2)}]} = \frac{3K_1^{\frac{1}{3}}}{K_2^{\frac{2}{3}}} - 1, \quad (21)$$



$$\lim_{a_1 \rightarrow 0} \frac{[RE_3^{1(1)2(2)}]^* - [RE_3^{1(1)2(2)}]}{[RE_3^{1(1)2(2)}]} = 0. \quad (22)$$

Table 2 gives an example of the effect of TIE on the distribution of isotopic molecules for deuterized ammonia ( $K_1 = 24.40$ ,  $K_2 = 24.08$  at  $298^\circ \text{K}$  from Zeise [6]).

TABLE 2. Effect of TIE on the Distribution of Isotopic Molecules in Deuterized Ammonia

Isotopic molecules	Maximum value of $(n^* - n)/n$ , %	Mole fraction from formula (2), n, % ( $a_1 = 0.5$ )	Mole fraction from formulas (18-19), $n^*$ , % ( $a_1 = 0.5$ )	$\frac{n^* - n}{n}$ , % ( $a_1 = 0.5$ )
NH <sub>3</sub>	12,1	12,5	12,8005	+2,404
NH <sub>2</sub> D	4,2	37,5	37,2458	-0,678
NHD <sub>2</sub>	2,8	37,5	37,1047	-1,054
ND <sub>3</sub>	10,6	12,5	12,8445	+2,756

Example 3.  $N = 4$ ,  $z = 2$ ,  $a_1$  is the atomic fraction of isotope  $E^1$  in element E. In this case five isotopic molecules can exist  $RE_4^{4(1)}$ ,  $RE_4^{3(1)1(2)}$ ,  $RE_4^{2(1)2(2)}$ ,  $RE_4^{1(1)3(2)}$ ,  $RE_4^{4(2)}$  and three independent equilibrium constants

$$K_1 = \frac{[RE_4^{3(1)1(2)}]^4}{[RE_4^{4(1)}]^3 [RE_4^{1(2)}]}; \quad K_2 = \frac{[RE_4^{2(1)2(2)}]^4}{[RE_4^{1(1)}]^2 [RE_4^{4(2)}]^2}; \quad K_3 = \frac{[RE_4^{1(1)3(2)}]^4}{[RE_4^{1(1)}] [RE_4^{4(2)}]^3}.$$

Eqs. (11) and (12) take the following form

$$\alpha + \left(1 - \frac{1}{4a_1}\right) K_3^{\frac{1}{4}} \alpha^{\frac{3}{4}} + \left(1 - \frac{2}{4a_1}\right) K_2^{\frac{1}{2}} \alpha^{\frac{2}{4}} + \left(1 - \frac{3}{4a_1}\right) K_1^{\frac{1}{4}} \alpha^{\frac{1}{4}} + \left(1 - \frac{1}{a_1}\right) = 0, \quad (23)$$

$$[RE_4^{4(1)}] = \frac{a_1}{1 + \frac{3}{4} K_1^{\frac{1}{4}} \alpha^{\frac{1}{4}} + \frac{2}{4} K_2^{\frac{1}{2}} \alpha^{\frac{2}{4}} + \frac{1}{4} K_3^{\frac{1}{4}} \alpha^{\frac{1}{4}}}. \quad (24)$$

Table 3 gives an example of the effect of TIE on the distribution of isotopic molecules in deuterized methane ( $K_1 = 145.2$ ,  $K_2 = 635.54$  and  $K_3 = 118.7$  at  $739^\circ$  from Ref. [7]).

TABLE 3. Effect of TIE on the Distribution of Isotopic Molecules and Deuterized Methane

Isotopic molecules	n, % at $a_1 = 0.5$ , mole fractions from (2)	$n^*$ , % at $a_1 = 0.5$ , mole fractions from (23,24)	$\frac{n^* - n}{n}$ , %
CH <sub>4</sub>	6,25	7,0857	+13,370
CH <sub>3</sub> D	25,00	24,8760	-0,496
CH <sub>2</sub> D <sub>2</sub>	37,50	36,4025	-2,930
CHD <sub>3</sub>	25,00	24,2165	-3,140
CD <sub>4</sub>	6,25	7,4193	+18,710

TABLE 4. Effect of TIE on the Distribution of Isotopic Molecules of Molecular Hydrogen Consisting of H, D and T

Isotopic molecule	Mole fraction n with out TIE, %	Mole fraction n* with TIE, %	$\frac{n^* - n}{n}$ , %
H <sub>2</sub>	11,111	12,664	+13,977
D <sub>2</sub>	11,111	11,208	+0,820
T <sub>2</sub>	11,111	12,068	+8,620
HD	22,222	21,511	-3,200
HT	22,222	19,818	-10,820
DT	22,222	22,731	+2,290

Element E Consists of Three Isotopes ( $z = 3$ ),  $x = 1$ .

The simultaneous solution of Eqs. (5), (6), (7) and (8) in general form for  $z = 3$  and  $N$  arbitrary encounters insuperable mathematical difficulties. Therefore, we shall consider only the case  $N = 2$ . Thus, the element E consists of three isotopes  $E^1$ ,  $E^2$  and  $E^3$  with atomic fraction  $a_1$ ,  $a_2$  and  $a_3$  ( $a_1 + a_2 + a_3 = 1$ ). In the present case it is possible to have

six different isotopic molecules:  $RE_2^{2(1)}$ ,  $RE_2^{2(2)}$ ,  $RE_2^{2(3)}$ ,  $RE_2^{1(1)1(2)}$ ,  $RE_2^{1(1)1(3)}$ ,  $RE_2^{1(2)1(3)}$  and three independent equilibrium constants

$$K_1 = \frac{[RE_2^{1(1)1(2)}]^2}{[RE_2^{2(1)}][RE_2^{2(2)}]}, \quad K_2 = \frac{[RE_2^{1(1)1(3)}]^2}{[RE_2^{2(1)}][RE_2^{2(3)}]} \quad \text{и} \quad K_3 = \frac{[RE_2^{1(2)1(3)}]^2}{[RE_2^{2(2)}][RE_2^{2(3)}]}.$$

It may be shown that after substitution

$$\left. \begin{aligned} [RE_2^{1(1)1(2)}] &= \alpha [RE_2^{2(1)}] \\ \text{and} \\ [RE_2^{1(1)1(3)}] &= \beta [RE_2^{2(1)}] \end{aligned} \right\} \quad (25)$$

the simultaneous solution of Eqs. (5), (7) and (8) [the number of Eq. (6) at  $x = 1$  is equal to 0] in this case is a matter of solving an equation of the fourth degree in  $\beta$

$$A\beta^4 + B\beta^3 + C\beta^2 + D\beta + E = 0, \quad (26)$$

where

$$\begin{aligned} A &= 1 - \frac{1}{4} K_3; \\ B &= \frac{1}{4} \sqrt{K_1 K_2 K_3} \left( \frac{1-2a_1}{a_1} \right) + K_2 \left( 1 - \frac{a_3}{a_1} \right) - \frac{K_2 K_3}{8} \left( \frac{1-2a_3}{a_1} \right); \\ C &= \frac{K_3}{8} \sqrt{K_1 K_2 K_3} \left( \frac{a_1 + a_3 - 2a_1^2 - 2a_3^2}{a_1^2} \right) + \frac{K_2^2}{4} \left( 1 - \frac{a_3}{a_1} \right)^2 + \\ &\quad + \frac{K_1 K_3}{4} \cdot \frac{a_3}{a_1} \left( 1 - \frac{a_3}{a_1} \right) - 2K_2 \frac{a_3}{a_1} + \frac{K_2 K_3}{4} \left( \frac{a_3 - a_2}{a_1} \right); \\ D &= \frac{K_3}{4} \sqrt{K_1 K_2 K_3} \frac{a_3(1-2a_3)}{a_1^2} - K_2 \left( 1 - \frac{a_3}{a_1} \right) \frac{a_3}{a_1} - \frac{K_1 K_2^2}{8} \cdot \frac{a_3(1-2a_1)}{a_1^3}; \\ E &= K_2^2 \frac{a_3^2}{a_1^2} \left( 1 - \frac{\beta}{4} K_1 \right). \end{aligned}$$

Having found the value of  $\beta$  from Eq. (26),  $\alpha$  is found from Eq. (27)

$$\alpha = - \left[ \frac{K_1}{4} \left( 1 - \frac{a_2}{a_1} \right) + \frac{\beta}{4} \sqrt{\frac{K_1 K_3}{K_2} \beta} \right] + \sqrt{\frac{K_1 K_3}{16 K_2} \beta^2 + \left[ \frac{K_1}{8} \left( 1 - \frac{a_2}{a_1} \right) \sqrt{\frac{K_1 K_3}{K_2}} + \frac{K_1}{2} \cdot \frac{a_2}{a_1} \right] \beta + \frac{K_1^2}{16} \left( 1 - \frac{a_2}{a_1} \right)^2 + K_1 \frac{a_2}{a_1}} \quad (27)$$

Then we find  $[RE_2^{2(1)}]$ :

$$[RE_2^{2(1)}] = \frac{a_1}{1 + \frac{\alpha}{2} + \frac{\beta}{2}}. \quad (28)$$

The values of  $[RE_2^{1(1)1(2)}]$  and  $[RE_2^{1(1)1(3)}]$  are found from Eqs. (28) and (25). The values of  $[RE_2^{2(2)}]$ ,  $[RE_2^{2(3)}]$  and  $[RE_2^{1(2)1(3)}]$  are found from the following relations:

$$\begin{aligned} [RE_2^{2(2)}] &= \alpha^2 [RE_2^{2(1)}] / K_1; \\ [RE_2^{2(3)}] &= \beta^2 [RE_2^{2(1)}] / K_2; \\ RE_2^{1(2)1(3)} &= \alpha \beta [RE_2^{2(1)}] \sqrt{\frac{K_3}{K_1 K_2}}. \end{aligned} \quad (29)$$

As an example we shall consider the case of molecular hydrogen consisting of three isotopes: H, D and T. Table 4 gives a comparison of the statistical distribution of the isotopic molecules calculated from formula (2), with the distribution of isotopic molecules corrected for TIE, for the case  $a_1 = a_2 = a_3 = 1/3$ . The following values were taken for the equilibrium constants at 298° K:  $K_1 = 3.26$ ,  $K_2 = 2.57$  and  $K_3 = 3.82$  [6]. It may be seen from Table 4 that the largest TIE is shown by protium. In the case of water the hydrogen of which consists of three isotopes (H, D and T) considerable TIE also occurs, since the values of  $K_1$ ,  $K_2$ , and  $K_3$  differ appreciably from 4 (the values of  $K_1$ ,  $K_2$  and  $K_3$  for the statistical distribution) and are equal at 298.1° K to 3.96, 3.42 and 3.59 respectively [6].

It is clear from the examples given that a considerable TIE always occurs with the hydrogen isotopes which, in the case of hydrogen, consisting of protium and tritium, reaches especially high values. In the case of heavier elements, the TIE in the distribution of isotopic molecules should have a smaller value, which is confirmed by the case of carbonic acid gas, consisting of the isotope  $C^{12}$ ,  $O^{16}$ , and  $O^{18}$ , and nitrous oxide consisting of the isotopes  $N^{14}$ ,  $N^{15}$ ,  $O^{16}$ . However, the TIE of molecular nitrogen, consisting of the isotopes  $N^{14}$  and  $N^{15}$ , has a very high value (11.11%). Thus, there is always the possibility that a considerable TIE may occur in the distribution of isotopic molecules of other light elements. Let us note in conclusion, that TIE causes a displacement of the distribution of isotopic molecules toward the formation of larger quantities of homoisotopic molecules on account of the reduction in the number of heteroisotopic molecules.

In conclusion I wish to express hearty thanks to Candidate in Chemical Sciences V. D. Nefedov for the interest he has shown in the present work, as well as note that this work represents a further development of the ideas presented to me by V.D. Nefedov.

#### SUMMARY

1. The thermodynamic isotope effect (TIE) may cause the distribution of isotopic molecules to differ substantially from the statistical distribution, especially in the case of light elements.
2. A method is indicated for setting up a system of algebraic equations, the solution of which makes it possible to calculate the concentration of isotopic molecules in any chemical compound consisting of any number of different isotopes.
3. A solution of the systems of algebraic equations is given for several simpler cases.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# ORGANIC AND BIOLOGICAL CHEMISTRY

## TAUTOMERISM AND GEOMETRIC ISOMERISM OF NITROGEN-CONTAINING DERIVATIVES OF CARBONYL COMPOUNDS

### COMMUNICATION 5. POLAROGRAPHIC STUDY OF SEMICARBAZONES AND THIOSEMICARBAZONES OF AROMATIC ALDEHYDES

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In previous communications [1-3] we presented the results of a polarographic study of semicarbazones and thiosemicarbazones of aliphatic-aromatic ketones. It was found that these semicarbazones and thiosemicarbazones exist in weakly acid and neutral methanolic-aqueous solutions in the form containing an azomethine grouping and are able to form stereochemical pairs under the action of ultraviolet radiation [2].

On the basis of the polarographic results we reached conclusions about the effect of substituents in the benzene nucleus, and also of the sulfur and oxygen atoms on the reactivity (ease of reduction) of the azomethine grouping [2]. By the method of polarographic coulometry it was shown that in the reduction of these compounds two electrons from the buffer solutions take part [1,3].

In continuation of our investigation of the structure and reactions of nitrogen-containing derivatives of carbonyl compounds we studied the polarographic behavior of the semicarbazones and thiosemicarbazones of benzaldehyde, p-isopropylbenzaldehyde, p-dimethylaminobenzaldehyde, salicylaldehyde, and o-, m-, and p-nitrobenzaldehydes in order to determine the state in which they exist in solution. As in the case of derivatives of aliphatic-aromatic ketones [1,3], the polarograms of solutions of the semicarbazones and thiosemicarbazones of aromatic aldehydes had sharp minima, whose depth depended on the depolarizer concentration and which disappeared on addition of agar-agar.

The dependence of the height of the reduction wave of the compounds studied on the pressure on the dropping mercury, and also on the temperature (in the range 15-50°), indicated that their reduction had the character of a diffusion process.

TABLE 1

Aldehyde	Temp. coeff. (% per 1°)	
	semi-carbazone	thiosemi-carbazone
Benzaldehyde	0.64	0.56
p-Isopropylbenzaldehyde	1.45	0.55
p-Dimethylaminobenzaldehyde	0.98	0.80
Salicylaldehyde	1.46	0.87
o-Nitrobenzaldehyde	1.00	0.83
m-Nitrobenzaldehyde	1.20	1.00
p-Nitrobenzaldehyde	1.30	1.20

The temperature coefficients of the derivatives of the isomeric nitrobenzaldehydes were calculated both from the nitro group wave and from the azomethine group wave. Their average values are given in Table 1. From this it will be seen that for the semicarbazones the temperature coefficients of the diffusion currents are greater than for the thiosemicarbazones, whereas for the derivatives of aliphatic-aromatic ketones we observed the reverse relation under the same polarography conditions. As a rule, all substances capable of being reduced by sodium amalgam in aqueous solution are reduced also at a dropping mercury electrode [4]. It is known [5] that the thiosemicarbazones of aromatic aldehydes give 1-aryl-3-thiosemicarbazides on reduction with sodium

amalgam, on the basis of which it would be expected that on reduction of semicarbazones and thiosemicarbazones at the dropping mercury electrode that 1-substituted semicarbazide or thiosemicarbazide will be formed. To verify this supposition we determined the number of electrons taking part in the reduction process by the method described in previous papers [1,6].

TABLE 2

Compound	pH	Amt $\cdot 10^{-6}$ that underwent elec- trolysis (mole)	$-E_v$ of electrolysis	$K \cdot 10^{-4}$ of electrolysis	No. of electrons
Benzaldehyde thio- semicarbazone	6.0	1.00	1.286	7.50	1.97
p-Isopropylbenzaldehyde thiosemicarbazone	6.0	0.40	1.250	4.62	1.80
p-Nitrobenzaldehyde semicarbazone	6.0	0.52	0.50	10.40	4.2
p-nitrobenzaldehyde semicarbazone	6.0	0.52	1.280	7.08	6.2

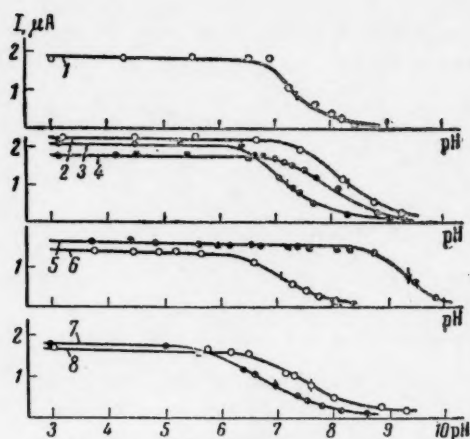


Fig. 1. Relation of the height of the wave for the reduction of the azomethine group to pH: 1) m-nitrobenzaldehyde semicarbazone; 2) p-nitrobenzaldehyde semicarbazone; 3) benzaldehyde semicarbazone; 4) p-isopropylbenzaldehyde semicarbazone; 5) p-dimethylaminobenzaldehyde thiosemicarbazone; 6) m-nitrobenzaldehyde thiosemicarbazone; 7) benzaldehyde thiosemicarbazone; 8) p-isopropylbenzaldehyde thiosemicarbazone.

thiosemicarbazones in a 0.08 M solution of  $(C_2H_5)_4NBr$  in 80% ethanol. Table 3 presents some of the results, which lead to the conclusion that in some of the compounds studied the azomethine group must be reduced in alkaline solutions at a dropping mercury electrode in the potential range from  $-1.8$  to  $-2.1$  v.

On reduction of the buffer capacity of the solution with maintenance of constant pH and ionic strength, the limiting current for the reduction of the azomethine group falls (Fig. 2). In unbuffered solutions the semicarbazones and thiosemicarbazones are not reduced. All these results show that, in buffer solutions, the azomethine group of semicarbazones and thiosemicarbazones forms a complex with a proton which is reduced at a dropping mercury electrode. However, as shown above, the limiting currents observed for the reduction of this group have a diffusional character, which is confirmed by the relation of the product of the wave height and the square root of the dropping period to the wave height (Fig. 3). The character of the variation of  $I \cdot \sqrt{t}$  with  $I$  indicates that the rate of protonization, which precedes the stage of the transfer of electrons, is fairly great and does not determine the over-all rate of the electrode process [4]. The points of inflection on the curves for the relation of wave height to the pH of the solution (see Fig. 1) correspond to the pH at which half of the molecules of the semicarbazones and thiosemicarbazones

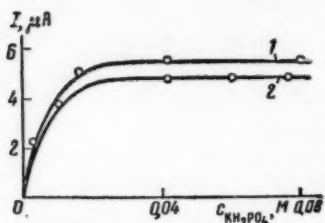
In Table 2 we give the results of a microcoulometric investigation, from which it follows that in the reduction of an azomethine group at the dropping mercury electrode the saturation of its double bond by the two-electron mechanism does in fact occur.

It can be seen also from Table 2 that in solutions of pH 6 the nitro group in the semicarbazones and thiosemicarbazones of nitrobenzaldehydes is reduced with the addition of four electrons. It should be noted that for different semicarbazones and thiosemicarbazones the limiting currents are approximately the same under identical conditions of polarography. This also confirmed the conclusion regarding the identical numbers of electrons required in their electroreduction.

It is a characteristic of the compounds studied that with rise in the pH of the solution the height of the wave of the azomethine group diminishes; the graphs for these relations, most of which are given in Fig. 1, are reminiscent of the dissociation curves of weak acids. At  $pH > 9$  the height of the wave of the azomethine group is almost zero, but on the polarograms of weakly alkaline solutions of the thiosemicarbazones of benzaldehyde and m-nitrobenzaldehyde and of the semicarbazones and thiosemicarbazones of salicylaldehyde a diffusion wave appears with a half-wave potential of about  $-1.8$  v and a height that is proportional to the depolarizer concentration. In presence of derivatives of p-isopropylbenzaldehyde the reduction of the base solution at  $pH \approx 9.2$  begins at a potential that is more positive (by 0.1 v) than in their absence. On the supposition that in this case also there is a polarographic wave that merges with the background we investigated several semicarbazones and



Compound	$-E_{H_2}, V$
Benzaldehyde semicarbazone	2.05
Benzaldehyde thiosemicarbazone	1.94
p-Dimethylaminobenzaldehyde semicarbazone	2.11
Salicylaldehyde semicarbazone	1.84; 2.20



Aldehyde	pK	
	semi-carbazone	thiosemi-carbazone
Benzaldehyde	7.20	6.95
p-Isopropylbenzaldehyde	8.00	7.65
p-Dimethylaminobenzaldehyde	9.05	9.40
m-Nitrobenzaldehyde	7.40	7.10
p-Nitrobenzaldehyde	8.30	8.25

$$\text{X-C}_6\text{H}_4\text{-C(=N-NH-C(=O)-NH}_2\text{)} + \text{H}^+ \rightleftharpoons \left[ \text{X-C}_6\text{H}_4\text{-C(=N-NH-C(=O)-NH}_2\text{)}^+ \right] \text{H}$$
$$[>C=N-]H^+ \xrightarrow[+e]{+H^+} [>\ddot{C}-NH-]H^+.$$

1654

TABLE 5

Aldehyde	Azomethine group				Nitro group			
	Semicarbazone		Thiosemicarbazone		Semicarbazone		Thiosemicarbazone	
	$\alpha n$	$\frac{dE_{1/2}}{dpH}$	$\alpha n$	$\frac{dE_{1/2}}{dpH}$	$\alpha n$	$\frac{dE_{1/2}}{dpH}$	$\alpha n$	$\frac{dE_{1/2}}{dpH}$
Benzaldehyde	0.060	0.086	0.056	0.060	—	—	—	—
p-Isopropylbenzaldehyde	0.060	0.084	0.048	0.060	—	—	—	—
p-Dimethylaminobenzaldehyde	0.054	0.082	0.048	0.074	—	—	—	—
m-Nitrobenzaldehyde	0.060	0.086	0.052	0.053	0.038	0.060	0.032	0.062
p-Nitrobenzaldehyde	0.058	0.088	0.048	0.072	0.030	0.060	0.033	0.058
o-Nitrobenzaldehyde	0.058	0.076	0.058	—	0.030	0.063	—	—
Salicylaldehyde	0.062	0.062	0.050	0.058	—	—	—	—

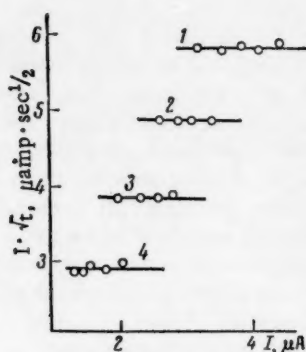


Fig. 3. Relation of  $I \cdot \sqrt{t}$  to  $I$ ; pH 6.0: 1) benzaldehyde semicarbazone; 2) p-dimethylaminobenzaldehyde semicarbazone; 3) p-nitrobenzaldehyde thiosemicarbazone ( $\text{NO}_2$  wave); 4) benzaldehyde thiosemicarbazone.

to alkaline solutions may be due to change in the mechanism of the reduction of the nitro group.

For the fuller investigation of the electrochemical behavior of semicarbazones and thiosemicarbazones at a dropping mercury electrode, in addition to the polarographic method we used the oscillographic method of determining the curves for the relation  $\frac{dE}{dt} = F(E)$  (the results of the oscillographic investigation will be published in a special communication). It was then found that the number of waves on the polarograms corresponds to the number of projections on the oscillograms for acid solutions of semicarbazones and thiosemicarbazones (Fig. 6). The polarographic reduction of a functional group may be represented as a nucleophilic-substitution reaction. On the basis of this several authors [4,8-10] have shown that Hammett's equation, which covers the rate constants and equilibrium constants for the nucleophilic substitution of aromatic compounds with p- or m-substituents [11,12], for an electrochemical reaction takes the form  $E_{1/2} - E_{1/2}^0 = \rho' \sigma$ , in which  $E_{1/2}^0$  and  $E_{1/2}$  are the half-wave potentials of the unsubstituted and substituted derivative, respectively;  $\rho'$  is a constant of the electrochemical reaction characterizing the susceptibility of the reaction center (group being reduced) to the effect of substituents;  $\sigma$  is a constant characterizing the effect of the given substituent in the benzene ring on the reactivity of the compound.

For irreversible reactions, in particular for irreversible polarographic reduction, Hammett's equation is valid

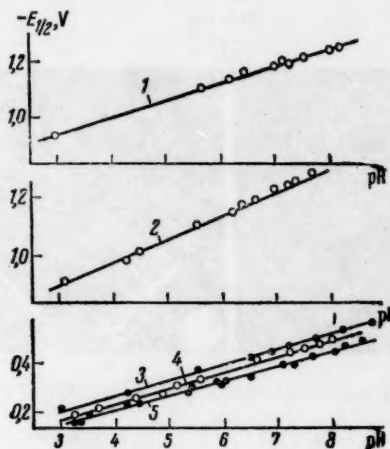


Fig. 4. Relation of the half-wave potential to pH: 1) p-isopropylbenzaldehyde thiosemicarbazone; 2) benzaldehyde semicarbazone; 3) m-nitro group (m-nitrobenzaldehyde semicarbazone); 4) m-nitro group (m-nitrobenzaldehyde thiosemicarbazone); 5) p-nitro group (p-nitrobenzaldehyde thiosemicarbazone).

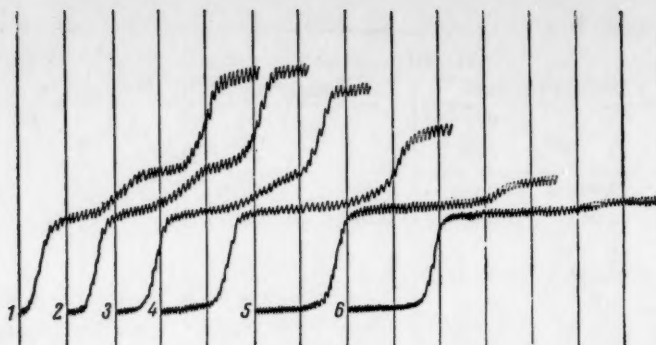


Fig. 5. Polarograms of solutions of *m*-nitrobenzaldehyde thiosemicarbazone; start of curves at  $-0.1$  v; spacing of abscissae 200 mv; sensitivity 1/20 at pH of: 1) 3.25; 2) 3.70; 3) 4.9; 4) 6.6; 5) 7.75; 6) 8.05.

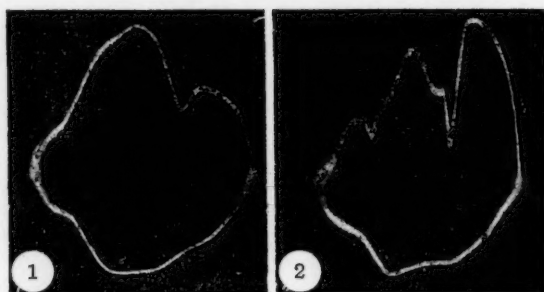


Fig. 6. Oscillopolarographic curves  $\frac{dE}{dt} = f(E)$ : 1) benzaldehyde semicarbazone (pH 5.8); 2) *p*-nitrobenzaldehyde semicarbazone (pH 1.0).

group, but of the hydroxyamino group. As will be seen from Fig. 7, for the semicarbazones and thiosemicarbazones there is a satisfactory linear relation between the half-wave potentials and the  $\sigma$  of the substituents, the values of which were taken from Jaffe's paper [12]. Some departures from the linear relation for derivatives of *p*-dimethylaminobenzaldehyde are probably to be explained on the view that the electron-donating  $(CH_3)_2N$  group participates in the conjugation with the bond being reduced via the  $\pi$ -bond system of the benzene nucleus, so that the polar effect of this group is weakened, i.e., the value of  $\sigma$  for the  $(CH_3)_2N$  group is reduced. An analogous interaction was observed for some *p*-amino benzene derivatives, for which Zuman [13] found a new value of  $\sigma$  from polarographic data.

From the slope of the straight line representing the relation of  $E_{1/2}$  to  $\sigma$  we determined the values of  $\rho'$ , the constant for the reduction of the protonized  $>C=N-$  bond. For the semicarbazones  $\rho'$  was found to 0.132, and for the thiosemicarbazones it was found to be 0.094. The value of  $\rho'$  for the semicarbazones of aromatic aldehydes is close to the value 0.12-0.13 found by Pearson for the semicarbazones of some benzophenones [8]. The values of  $\rho'$  that we found are relatively low, i.e., the effect of the substituent on the reduction of the azomethine group in the compounds studied is comparatively slight.

The electronic structures of all the compounds investigated were characterized by  $\pi p/\pi$  conjugation and a relatively high mobility of the nonlocalized electron cloud of the molecule. As the azomethine bond being reduced is at the end of the conjugated chain and is only one of the transmitting links in that chain, under the influence of one or other substituent in the phenyl ring of the original aldehyde its electron density changes only slightly, which explains the fairly close values of the half-wave potentials of the derivatives of substituted and unsubstituted carbonyl compounds. Semicarbazones and thiosemicarbazones have the electronegative oxygen and sulfur atoms at the end of

only when data for a series of derivatives are obtained under completely identical conditions. As the reduction of the azomethine group in the semicarbazones and thiosemicarbazones of aromatic aldehydes proceeds by one single mechanism, which is also a necessary condition for the applicability of Hammett's equation [13], our results were used for the quantitative evaluation of the effect of substituents on the electrochemical reduction of the semicarbazones and thiosemicarbazones [14]. From the exact values of the half-wave potentials at pH 6.0 we plotted graphs in the coordinates  $E_{1/2}$  and  $\sigma$  (in Hammett units).

As the nitro group in the derivatives of *p*- and *m*-nitrobenzaldehydes is reduced at pH 6.0 to hydroxyamino, we examined the effect on the polarographic reduction of the  $>C=N-$  bond in these derivatives not of the nitro

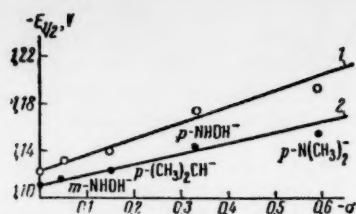
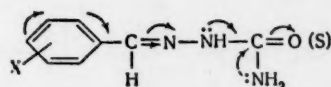


Fig. 7. Relation of the half-wave potential on the  $\sigma$  of the substituent: 1) semicarbazones; 2) thiosemicarbazones.

TABLE 6

Substituent	$-E_{1/2}$ , V		$\sigma$	
	para	meta	para	meta
$\begin{array}{c} \text{—} \\ \text{—C=N—NH—C=O} \\   \quad \quad   \\ \text{H} \quad \quad \text{NH}_2 \end{array}$	0,480		0	
	0,350	0,373	+0,81	+0,67
$\begin{array}{c} \text{—} \\ \text{—C=N—NH—C=S} \\   \quad \quad   \\ \text{H} \quad \quad \text{NH}_2 \end{array}$	0,350	0,378	+0,81	+0,64

the conjugated chain, and the direction in which these act on the molecule is in accord with the direction of the polarization of the  $>\text{C}=\text{N}-$  bond and with the effect of electron-donating substituents in the phenyl nucleus, and it brings about a displacement of the nonlocalized electron cloud in the direction of the oxygen or sulfur atom.



This displacement is greater for semicarbazones, for oxygen, being more electronegative than sulfur, causes a greater lack of symmetry in the electron cloud of the conjugated bonds of the molecules and acts more strongly on the electron density of the azomethine group. Hence, the effect of the substituent is greater in semicarbazones than in thiosemicarbazones.

The derivatives of the isomeric nitrobenzaldehydes that we studied may be regarded in the same way as substituted aromatic nitro compounds. Our results therefore allow us to solve the inverse problem: to calculate the value of  $\sigma$  for the semicarbazone and thiosemicarbazone substituents on the basis of the reaction of electrochemical reduction of the nitro group. Table 6 gives values of  $\sigma$  for these substituents calculated from the difference of the half-wave potentials of substituted and unsubstituted nitrobenzenes on the assumption that  $\rho'$  is 0.16 [9].

The values of  $\sigma$  found for the semicarbazone and thiosemicarbazone substituents were very close, i.e., they have almost the same effect, transmitted through the  $\pi$ -bond system of the benzene ring, on the reduction of the nitro group, which is evidence of the similarity of the electronic structures of these substituents to a  $\pi\pi$ -conjugated system of bonds having a nonlocalized electron cloud of relatively high mobility. It must be pointed out that the values of  $\rho'$  and  $\sigma$  cited in the present work are tentative, since they were obtained in a study of a few compounds and will undoubtedly require correction.

Hammett's equation may be used also for the study of the stability of the above-discussed protonized complex formed in the reaction layer adjacent to the electrode, because the structure of the molecule must have a definite influence on this stability. The existence of a connection between the stability of the protonized complex and the effect of substituents in the benzene ring is supported by the fact that the values of the  $pK$  for the instability of protonized complexes, given in Table 4, and the  $\sigma$  values of the substituents of the corresponding semicarbazone and thiosemicarbazone are related linearly (Fig. 8). The action of electron-donating substituents in the benzene nucleus, leading to a displacement of the nonlocalized electron cloud in the direction of the nitrogen atom of the azomethine group, increases its negative charge and consequently increases the basicity of the semicarbazones and thiosemicarbazones. Hence, by applying Hammett's equation we are able to obtain a quantitative estimate of the effect of the structure of the azomethine derivatives studied (in the present case of the nature and position of the substituent), on the stability of the transitional complex in the electrochemical reaction.

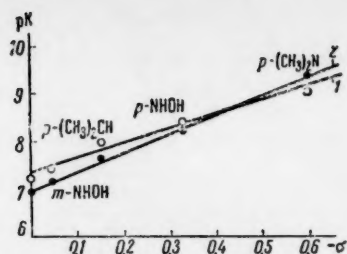


Fig. 8. Relation of the  $pK$  for the instability of protonized complexes to the value of  $\sigma$  of the substituent: 1) semicarbazones; 2) thiosemicarbazones.



# EXPERIMENTAL

The semicarbazones and thiosemicarbazones used in the work were prepared by the usual methods, as recommended in the literature; their purities were judged from their melting points (Table 7).

TABLE 7

Aldehyde	Melting point (°C)	
	Semicarbazone	Thiosemicarbazone
Benzaldehyde	220 (222)*	159 (160)
p-Isopropylbenzaldehyde	208 (210)	144
p-Dimethylamino-benzaldehyde	219 (222)	197-198
m-Nitrobenzaldehyde	246 (246)	229 (229)
p-Nitrobenzaldehyde	211 (211)	228
o-Nitrobenzaldehyde	237 (242)	225
Salicylaldehyde	225 (225)	226 (231)

\* In parentheses we give values of melting point taken from the literature (e.g., [15]); it must be pointed out that in some cases the values for some of the semicarbazones and thiosemicarbazones taken from different sources differ from one another.

dropping mercury electrode is explained from the point of view of modern concepts on the structure of organic compounds.

The procedure used in the polarographic and microcoulometric investigation of semicarbazones and thiosemicarbazones has been described by us previously [1,2]. These compounds were studied in 20% methanolic-aqueous solutions at a concentration of  $3 \cdot 10^{-4}$  M with a base solution of citrate-phosphate buffers. The pH was measured with an LP-5 electron-tube pH meter.

## SUMMARY

1. A study was made of the polarographic behavior of the semicarbazones and thiosemicarbazones of benzaldehyde, p-isopropylbenzaldehyde, p-dimethylaminobenzaldehyde, salicylaldehyde, and o-, m-, and p-nitrobenzaldehydes, and it was shown that two electrons take part in their reduction.

2. The effect of the structures of semicarbazones and thiosemicarbazones on the ease of reduction at a

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## PREPARATION OF (ETHYLCYCLOPENTADIENYL) MANGANESE TRICARBONYL

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The only previous reference to the preparation of (ethylcyclopentadienyl) manganese tricarbonyl is a brief description in a patent [1] to its preparation from ethylcyclopentadiene in a way similar to that used for cyclopentadienylmanganese tricarbonyl; its boiling point and refractive index are given. For the preparation of (ethylcyclopentadienyl) manganese tricarbonyl we used the method indicated in the patent, but the absence of complete information on this prompted us to describe it together with a second method that we used for the preparation of this substance: alkylation of cyclopentadienylmanganese tricarbonyl with ethyl bromide in presence of aluminum chloride.

We carried out the alkylation of cyclopentadienylmanganese tricarbonyl with ethyl bromide by the Friedel-Crafts method in absence of solvent. It was shown that under certain conditions it is possible to obtain only the mono-ethyl derivative in 63% yield on the amount of cyclopentadienylmanganese tricarbonyl that reacts. From (ethylcyclopentadienyl) manganese tricarbonyl we prepared its acetyl and benzoyl derivatives, from which we prepared the corresponding 2,4-dinitrophenylhydrazones. The acylation of (ethylcyclopentadienyl) manganese tricarbonyl was carried out in presence of aluminum chloride and in absence of solvent.

### EXPERIMENTAL

The experiments on the preparation of ethylcyclopentadiene and ethylcyclopentadienylsodium, on the alkylation of cyclopentadienylmanganese tricarbonyl, and on the acylation of (ethylcyclopentadienyl) manganese tricarbonyl were carried out in a 250-ml flask fitted with stirrer, dropping funnel, reflux condenser, and tube for the passage of nitrogen. All reactions were carried out in a pure nitrogen atmosphere.

**Reaction of Ethylcyclopentadienylsodium with Manganese Dichloride and Carbon Monoxide**

**Ethylcyclopentadiene.** With continuous stirring 43.6 g (0.4 mole) of ethyl bromide was added dropwise at 0° to a solution of cyclopentadienylsodium in tetrahydrofuran prepared from 28.75 g (0.435 mole) of monomeric cyclopentadiene with 10 g (0.435 mole) of suspended sodium in 100 ml of tetrahydrofuran. When the addition of the ethyl bromide was complete, cooling ceased to be applied to the mixture, but stirring was continued. When the temperature of the mixture rose to that of the room, the solution of ethylcyclopentadiene in tetrahydrofuran was filtered by suction from the sodium bromide into two successive traps cooled by a mixture of acetone and solid carbon dioxide and was then left overnight at -70°. The solution of ethylcyclopentadiene in tetrahydrofuran was used further for the preparation of ethylcyclopentadienylsodium.

**Ethylcyclopentadienylsodium.** With stirring the solution of ethylcyclopentadiene in tetrahydrofuran was added in portions (3 × 50 ml) at room temperature to a suspension of 7 g (0.3 mole) of sodium in 25 ml of tetrahydrofuran. A solution of ethylcyclopentadienylsodium in tetrahydrofuran is yellow.

**(Ethylcyclopentadienyl) manganese Tricarbonyl.** A 250-ml rotating autoclave was charged with 18 g (0.143 mole) of manganese chloride, some steel balls for agitation purposes, and 180 ml of the solution of ethylcyclopentadienylsodium (0.3 mole) in tetrahydrofuran. Carbon monoxide was passed in up to a pressure of 100 atm, the autoclave was rotated, and the mixture was heated at 180° for four hours (until carbon monoxide ceased to be absorbed). Steam distillation of the reaction mixture gave 27.5 g of a dark-yellow oil, which was heavier than water; from this, by chromatography on silica gel, we isolated 18.25 g (55% on the manganese chloride taken) of (ethylcyclopentadi-

enyl) manganese tricarbonyl;  $n_D^{20}$  1.5760;  $d_4^{20}$  1.3298. Found: H 3.90; 3.92; C 52.05; 52.19; Mn 23.14; 23.14%;  $C_{10}H_9O_3Mn$ . Calculated: H 3.88; C 51.80; Mn 23.0%.

#### Alkylation of Cyclopentadienylmanganese Tricarbonyl with Ethyl Bromide in Presence of Aluminum Chloride

A mixture of 10 g (0.049 mole) of cyclopentadienylmanganese tricarbonyl and 7.84 g (0.059 mole) of aluminum chloride was heated to 80°. The layer of the dark-red liquid mixture formed was stirred continuously while dropwise addition was made of 5.34 g (0.048 mole) of ethyl bromide. When the addition of ethyl bromide was complete, the mixture was cooled and poured into ice water acidified with hydrochloric acid. The reaction mixture was washed with distilled water and steam-distilled. The original carbonyl was separated from the liquid (ethylcyclopentadienyl) manganese tricarbonyl by filtration through a No. 3 glass filter and fractionation under a high vacuum (20° at  $1.5 \cdot 10^{-2}$  mm). We isolated 3.53 g (63% on the cyclopentadienylmanganese tricarbonyl that reacted) of (ethylcyclopentadienyl) manganese tricarbonyl ( $n_D^{20}$  1.5760;  $d_4^{20}$  1.3290). The amount recovered of the original carbonyl was 5.1 g (51%). Found: H 4.13; 3.29; C 52.22; 51.98; Mn 23.26; 23.24%.  $C_{10}H_9O_3Mn$ . Calculated: H 3.88; C 51.80; Mn 23.0%.

(Ethylcyclopentadienyl) manganese tricarbonyl is a light-yellow liquid, readily soluble in heptane, ether, and acetone.

#### Acylation of (Ethylcyclopentadienyl) Manganese Tricarbonyl

(Acetylcyclopentadienyl) manganese Tricarbonyl. With stirring 7 g (0.03 mole) of (ethylcyclopentadienyl) manganese tricarbonyl was added to 13.33 g (0.1 mole) of aluminum chloride. A thick suspension was formed, and with continuous stirring at room temperature 2.37 g (0.03 mole) of acetyl chloride was added dropwise. Reaction proceeded with the evolution of much heat. When the addition of acetyl chloride was complete, the reaction mixture was heated and kept at 50° for four hours. The reaction mixture was cooled, decomposed with ice water acidified with hydrochloric acid, and steam-distilled. After being dried over  $MgSO_4$  the substance was vacuum-fractionated ( $1.5 \cdot 10^{-2}$  mm). We isolated 5.11 g (62.2%) of (acetylcyclopentadienyl) manganese tricarbonyl;  $n_D^{20}$  1.5820;  $d_4^{20}$  1.3441. Found: H 4.17; 4.13; C 52.87; 52.86%.  $C_{12}H_{11}O_4Mn$ . Calculated: H 4.01; C 52.59%.

(Acetylcyclopentadienyl) manganese tricarbonyl is a dark-yellow liquid which becomes dark brown when exposed to light; it is soluble in organic solvents (heptane, carbon tetrachloride, acetone). With 2,4-dinitrophenylhydrazine it gives a light-red crystalline 2,4-dinitrophenylhydrazone, m.p. 179°. Found: H 3.23; 3.19; C 47.42; 47.43; N 12.23; 12.56%.  $C_{18}H_{15}N_4O_7Mn$ . Calculated: H 3.33; C 47.60; N 12.33%.

(Benzoylcyclopentadienyl) manganese Tricarbonyl. With stirring 21.3 g (0.09 mole) of (ethylcyclopentadienyl) manganese tricarbonyl was added to 38.7 g (0.29 mole) of aluminum chloride, and then dropwise addition was made of 13.3 g (0.095 mole) of benzoyl chloride. Reaction went with the evolution of heat. When the addition of benzoyl chloride was complete, the reaction mixture was heated and kept at 80° for one hour (until hydrogen chloride ceased to be evolved). The mixture was then decomposed with ice water acidified with hydrochloric acid, washed with water, dried over  $MgSO_4$ , and vacuum-distilled ( $2 \cdot 10^{-3}$  mm). We isolated 24.88 g (82.3%) of (benzoylcyclopentadienyl) manganese tricarbonyl;  $n_D^{20}$  1.6219;  $d_4^{20}$  1.3404. Found: H 3.94; 3.83; C 60.93; 60.90%.  $C_{17}H_{13}O_4Mn$ . Calculated: H 3.91; C 60.72%.

(Benzoylcyclopentadienyl) manganese tricarbonyl is a thick orange liquid which becomes dark brown when exposed to light; it does not distill in steam, and it dissolves in organic solvents (heptane, carbon tetrachloride, acetone). With 2,4-dinitrophenylhydrazine it gives a dark-red crystalline 2,4-dinitrophenylhydrazone, m.p. 138-138.5°. Found: H 3.22; 3.15; C 53.13; 53.47; N 10.68; 10.64%.  $C_{23}H_{17}N_4O_7Mn$ . Calculated: H 3.32; C 53.50; N 10.85%.

#### SUMMARY

1. (Ethylcyclopentadienyl) manganese tricarbonyl was prepared in two ways: reaction of ethylcyclopentadienyl-sodium with manganese dichloride and carbon monoxide, and Friedel-Crafts alkylation of cyclopentadienylmanganese tricarbonyl.
2. By the acylation of (ethylcyclopentadienyl) manganese tricarbonyl, (acetylcyclopentadienyl) manganese and (benzoylcyclopentadienyl)manganese tricarbonyls were prepared.

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# SYNTHESIS AND STUDY OF THE REACTIVITY OF POLYMERIZABLE ORGANOMETALLIC DERIVATIVES OF p-VINYLBENZOIC ACID

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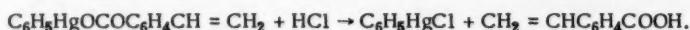
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As yet, inadequate study has been devoted to the organometallic derivatives of organic acids [1-3]. It was therefore considered to be of interest to synthesize some organometallic derivatives of p-vinylbenzoic and benzoic acids and to investigate their reactivities under comparable conditions. With this object we prepared the following organometallic compounds for the first time:

- 1) triphenyltin p-vinylbenzoate  $(C_6H_5)_3SnOCOC_6H_4CH=CH_2$ ;
- 2) triphenyltin benzoate  $(C_6H_5)_3SnOCOC_6H_5$ ;
- 3) triphenyllead p-vinylbenzoate  $(C_6H_5)_3PbOCOC_6H_4CH=CH_2$ ;
- 4) triphenyllead benzoate  $(C_6H_5)_3PbOCOC_6H_5$ ;
- 5) diphenylantimony p-vinylbenzoate  $(C_6H_5)_2SbOCOC_6H_4CH=CH_2$ ;
- 6) diphenylantimony benzoate  $(C_6H_5)_2SbOCOC_6H_5$ ;
- 7) phenylmercury p-vinylbenzoate  $C_6H_5HgOCOC_6H_4CH=CH_2$ ;
- 8) phenylmercury benzoate  $C_6H_5HgOCOC_6H_5$ .

Reaction with HCl. At from  $-5^\circ$  to  $-10^\circ$  phenylmercury p-vinylbenzoate readily reacts with alcoholic HCl with formation in 75% yield of phenylmercury chloride and p-vinylbenzoic acid in accordance with the equation



Under the same conditions phenylmercury benzoate gives a 100% yield of phenylmercury chloride and benzoic acid. Hence, under comparable conditions the benzoate radical  $C_6H_5COO$  is more reactive than the vinylbenzoate radical  $CH_2=CHC_6H_4COO$ . At from  $-5^\circ$  to  $-10^\circ$  triphenyllead p-vinylbenzoate readily reacts with alcoholic HCl with formation in 73-77% yield of triphenyllead chloride and p-vinylbenzoic acid according to the equation:



Under similar conditions triphenyllead benzoate gives an 80% yield of triphenyllead chloride and benzoic acid. These results show that the difference found in the reactivities of the  $C_6H_5COO$  and  $CH_2=CHC_6H_4COO$  radicals for the case of mercury compounds is found also in the corresponding lead compounds with the difference that with the accumulation of phenyl groups in the molecule of the organometallic compound the difference between the reactivities of these radicals becomes less.

Polymerization of Organometallic Derivatives of p-vinylbenzoic Acid. The organometallic derivatives of p-vinylbenzoic acid readily polymerize in the mass and in solution in presence of initiators for free-radical polymerization, or in the absence of these with heating to  $80-150^\circ$ . The mass-polymers are clear colorless or slightly yellow thermoplastic solids, insoluble in the usual organic solvents. To study the reactivity of the organometallic derivatives of p-vinylbenzoic acid we studied the kinetics of radical polymerization in toluene in presence of 0.25% by weight of azobisisobutyronitrile at  $80^\circ$ ,  $90^\circ$ , and  $100^\circ$  by the dilatometric method (Fig. 1). The investigation showed that with respect to rate of polymerization the organometallic derivatives of p-vinylbenzoic acid studied form the following series: phenylmercury p-vinylbenzoate > triphenyltin p-vinylbenzoate > triphenyllead p-vinylbenzoate > diphenylantimony p-vinylbenzoate > p-vinylbenzoic acid. This shows that phenylmercury p-vinylbenzoate polymerizes most readily and unsubstituted p-vinylbenzoic acid polymerizes most slowly. It was thus shown that the introduction of organometallic substituents containing phenyl groups into the p-vinylbenzoic acid molecule leads to

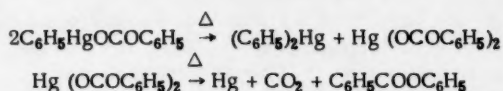


an increase in the rate of polymerization and depending on the identity of the metal we obtain the following series: Hg > Sn > Pb > Sb.

**Thermal Stability of Polymers of Organometallic Derivatives of p-Vinylbenzoic Acid.** With the object of studying the effect of the nature of the metal in the organometallic derivative of p-vinylbenzoic acid on the thermal stability of its polymers, we studied their degradation at 150°, 200° and 250°.

It was found that in the degradation of organometallic derivatives of p-vinylbenzoic acid there occurred disproportionation with formation of aryl derivatives of mercury, lead, and tin (diphenylmercury, tetraphenyllead, and tetraphenyltin) and new metal-containing polymers of higher thermal stability. In thermal stability the organometallic polymers studied formed the following series: triphenyltin p-vinylbenzoate > diphenylantimony p-vinylbenzoate > triphenyllead p-vinylbenzoate > phenylmercury p-vinylbenzoate, the most thermostable being the polymer of triphenyltin p-vinylbenzoate (Table 1). These results show that, as a function of the nature of the metal, the thermal stabilities of the polymers studied may be placed in the following series: Sn >> Sb > Pb > Hg.

**Thermal Decomposition of the Benzoates of Phenyl Derivatives of Hg, Pb, Sn, and Sb.** In confirmation of these results we studied the thermal decomposition of the benzoates of phenyl derivatives of mercury, lead, tin, and antimony under comparable conditions at 150-250°. Disproportionation occurred with formation of aryl derivatives of the metals (diphenylmercury, tetraphenyllead, and tetraphenyltin) and the corresponding benzoic salts, which decomposed further in the course of the heating. One of the decomposition products was phenyl benzoate, as can be seen for the case of phenylmercury benzoate:



In the case of the decomposition of diphenylantimony benzoate we observed the formation of organoantimony compounds of unestablished structure together with phenyl benzoate. As in the case of the metal-containing polymers of p-vinylbenzoic acid, the most stable compound was the triphenyltin derivative (Table 2). These data show that the rate of decomposition of the benzoates depends on the nature of the metal Sn > Sb > Pb > Hg, i.e., phenylmercury benzoate decomposes the most readily.

TABLE 1. Thermal Decomposition of Polymers of Organometallic Derivatives of p-Vinylbenzoic Acid

Formula	Loss in wt. % after 3 hr at			Analysis of residue after heating at 250°					
	200°	250°	300°	C, %		H, %		M, %	
				before	after	before	after	before	after
$(C_6H_5)_3SnOCOC_6H_4CH=CH_2$	—	6,6	26,7	65,19	48,21	4,43	3,87	23,94	31,88
$(C_6H_5)_3PbOCOC_6H_4CH=CH_2$	15,06	28,1	—	55,38	38,11	3,76	3,29	35,38	49,90
$(C_6H_5)_3SbOCOC_6H_4CH=CH_2$	15,0	21,8	—	59,57	43,53	4,02	3,45	—	—
$C_6H_5HgOCOC_6H_4CH=CH_2$	13,8*	39,0*	—	42,49	43,76	2,82	3,09	—	—

\* Metallic mercury was liberated.

A comparison of the results of the study of the decomposition of the benzoates of phenyl derivatives of Hg, Pb, Sn, and Sb with the thermostabilities of the polymers of organometallic derivatives of p-vinylbenzoic acid shows the generality of the regularities observed. The p-vinylbenzoic and benzoic derivatives of phenyl Hg, Pb, Sn, and Sb have different thermostabilities depending on the nature of the metal present, namely Sn > Sb > Pb > Hg, i.e., the most thermostable are the organotin compounds.

#### EXPERIMENTAL \*

**Synthesis of p-Vinylbenzoic Acid.** A solution of 13.8 g (0.1 mole) of p-chlorostyrene in 50 ml of tetrahydrofuran was added over a period of 30 minutes to 2.4 g (0.1 g-atom) of activated magnesium, and the reaction mixture was then heated at 60° for 15 minutes and stirred for 45 minutes at room temperature. External cooling was

\* I. L. Arkhipova took part in the experimental work.



TABLE 2. Thermal Decomposition of Polymers of Organometallic Derivatives of Benzoic Acid

Formula	Loss in wt. (%) after 3 hr at			Notes
	150°	200°	250°	
$(C_6H_5)_3SnOCOC_6H_5$	—	—	14.92	$(C_6H_5)_4Sn$ was liberated
$(C_6H_5)_3PbOCOC_6H_5$	—	—	37.13	$(C_6H_5)_4Pb$ was liberated
$(C_6H_5)_2SbOCOC_6H_5$	—	13.73	27.48	—
$C_6H_5HgOCOC_6H_5$	7.6	27.2	—	Metallic Hg was liberated

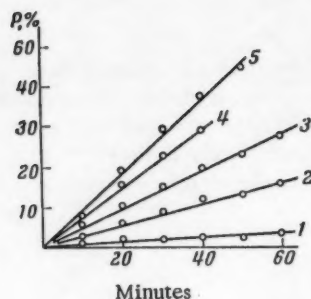


Fig. 1. Kinetics of the polymerization of organometallic derivatives of p-vinylbenzoic acid: 1) p-vinylbenzoic acid at 100°; 2) diphenylantimony p-vinylbenzoate at 90°; 3) triphenyllead p-vinylbenzoate at 90°; 4) triphenyltin p-vinylbenzoate at 90°; 5) phenylmercury p-vinylbenzoate at 100°.

applied, and solid carbon dioxide was added to the reaction mixture; this was followed by dilute sulfuric acid. The p-vinylbenzoic acid formed was extracted with ether and crystallized from 20% aqueous ethanol. Yield 5.3 g (36%); m.p. 138-140° (in a sealed capillary). The literature [4] gives m.p. 139-140°. At the same time a large amount of polymeric material was formed.

**Triphenyltin p-Vinylbenzoate.** A solution of 3.67 g (0.01 mole) of triphenyltin hydroxide in 30 ml of ether was added dropwise to a solution of 1.48 g (0.01 mole) of p-vinylbenzoic acid in 30 ml of ether. After stirring for one hour, ether was removed. We obtained 4.7 g (95%) of colorless crystals, m.p. 81-83°. Found: C 65.52; 65.56; H 4.78; 4.86; Sn 23.83; 24.00%.  $C_{27}H_{22}O_2Sn$  calculated: C 65.19; H 4.43; Sn 23.94%.

**Triphenyllead p-Vinylbenzoate.** This was prepared from 4.5 g of triphenyllead hydroxide and 1.48 g of p-vinylbenzoic acid in alcoholic solution by heating the mixture for one hour. After two crystallizations from hexane we obtained 3.0 g (51.7%) of colorless crystals, m.p. 136-138°. Found: C 55.51; H 4.12 3.96; Pb 35.16; 35.65%.  $C_{27}H_{22}O_2Pb$ . Calculated: C 55.38; H 3.76; Pb 35.38%.

**Diphenylantimony p-Vinylbenzoate.** This was prepared analogously from 5.68 g of diphenylantimony oxide and 3.0 g of p-vinylbenzoic acid in alcoholic solution. Two crystallizations from petroleum ether gave 5.4 g (64.5%) of colorless crystals, m.p. 78-80°. Found: C 59.49; H 4.56; Sb 28.92%.  $C_{21}H_{17}O_2Sb$ . Calculated: C 59.57; H 4.02; Sb 28.84%.

**Triphenyltin Benzoate.** This was prepared from triphenyltin hydroxide (0.01 mole) and benzoic acid (0.01 mole) in ethanol solution with heating at 70° for 30 minutes. We obtained a 95% yield of colorless crystals, m.p. 70-72° (from alcohol). Found: Sn 26.03%.  $C_{25}H_{20}O_2Sn$ . Calculated: Sn 25.27%.

**Triphenyllead Benzoate.** This was prepared analogously. We obtained a 90% yield of colorless crystals, m.p. 117-120° (from alcohol). Found: Pb 36.75.  $C_{25}H_{20}O_2Pb$ . Calculated: Pb 30.03%.

**Diphenylantimony Benzoate.** This was prepared from diphenylantimony oxide and benzoic acid, as indicated above. We isolated colorless crystals, m.p. 121-122°, in 75.5% yield. Found: Sb 30.85%.  $C_{19}H_{15}O_2Sb$ . Calculated: Sb 30.73%.

**Phenylmercury Benzoate.** This had m.p. 96-97° (from alcohol). The literature [5] gives m.p. 97-98°. Found: Hg 50.19%.  $C_{13}H_{10}O_2Hg$ . Calculated: Hg 50.32%.

**Reaction of Organometallic Derivatives of p-Vinylbenzoic Acid and of Benzoic Acid with HCl, Alcoholic HCl** (4 ml) was added to 0.5 g of the organometallic derivative of p-vinylbenzoic acid. The reaction mixture was kept for one hour at a temperature between -10° and +20° and then treated with water. The insoluble precipitate was filtered off, dried, recrystallized, and analyzed for metal content. From the aqueous-alcoholic solution p-vinylbenzoic acid separated and was identified by its melting point. With alcoholic HCl at from -5° to -10° phenylmercury benzoate gave a quantitative yield of phenylmercury chloride, m.p. 250-251°, and benzoic acid. Under the same conditions triphenyllead benzoate gave a 79-80% yield of triphenyllead chloride, m.p. 204°. The literature [6] gives m.p. 208°.

With alcoholic HCl at  $-10^{\circ}$  phenylmercury p-vinylbenzoate gave p-vinylbenzoic acid and phenylmercury chloride in a yield of 59% (at  $-10^{\circ}$ ) or 76% (at  $-5^{\circ}$ ). Under the same conditions triphenyllead p-vinylbenzoate gave triphenyllead chloride in a yield of 73% (at  $-10^{\circ}$ ) or 77% (at  $-5^{\circ}$ ).

Polymerization of Organometallic Derivatives of p-Vinylbenzoic Acid. The p-vinylbenzoates of the phenylated derivatives of Hg, Pb, Sn, and Sb were polymerized in sealed tubes in absence of initiator in the mass at  $100^{\circ}$ ,  $130^{\circ}$ , and  $150^{\circ}$ ; this gave colorless or yellow thermoplastic solids, insoluble in organic solvents. The conversion of monomer into polymer amounted to 75-90%. In presence of 0.3% of azobisisobutyronitrile as initiator the polymerization of the same monomers proceeded at  $100^{\circ}$  with the same conversion. The kinetics of the polymerization of organometallic derivatives of p-vinylbenzoic acid were studied by the dilatometric method in 0.3 M toluene solution in presence of 0.25% by weight of azobisisobutyronitrile as initiator. The polymerization of phenylmercury p-vinylbenzoate was studied in 0.1 M toluene solution. The results of the experiments on polymerization are presented in the graph in Fig. 1.

Study of the Thermal Stabilities of Organometallic Derivatives of p-Vinylbenzoic Acid. Samples of polymer obtained by thermal mass polymerization were extracted with benzene to remove traces of monomers and vacuum-dried at  $60^{\circ}$  to constant weight. A 0.5-g sample of the polymer was placed in a 5-ml flask connected to traps cooled with liquid nitrogen and was heated in Wood's metal for three hours at  $150-300^{\circ}$ . The course of the degradation of the polymer was followed from the loss in weight and the change in color. The results are presented in Table 1.

A study of the rate of decomposition of organometallic derivatives of benzoic acid was made under similar conditions. The results of the investigation are presented in Table 2.

The formation of tetraphenyllead and of tetraphenyltin was proved by the melting points and the elementary analyses.

#### SUMMARY

1. Organometallic derivatives of p-vinylbenzoic acid were synthesized for the first time.
2. In the reaction of organometallic derivatives of p-vinylbenzoic and of benzoic acids with HCl the radical  $C_6H_5COO$  is more reactive than the radical  $CH_2 = CHC_6H_4COO$ .
3. Organometallic derivatives of p-vinylbenzoic acid polymerize at different rates, depending on the nature of the metal:  $Hg > Sn > Pb > Sb$ .
4. The thermal stability of polymers of organometallic derivatives of p-vinylbenzoic acid also depends on the nature of the metal:  $Sn > Sb > Pb > Hg$ . The polymer of triphenyltin p-vinylbenzoate is the most thermostable.

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# TELOMERIZATION OF DIMETHYLCYCLOSILOXANES

## COMMUNICATION 3. TELOMERIZATION REACTIONS WITH DICHLOROMETHYLVINYLSILANE AND DICHLOROMETHYL- PHENYLSILANE

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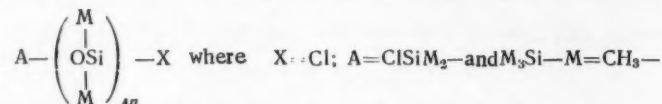
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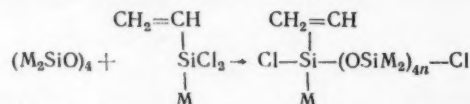
Original article submitted March 23, 1961

In previous communications it was reported that dimethylcyclotetrasiloxanes react with dichlorodimethylsilane [1-3] and with chlorotrimethylsilane with formation of oligomers of general formula



In the present communication we describe the telomerization of octamethylcyclotetrasiloxane with dichloromethylvinylsilane and with dichloromethylphenylsilane. In carrying out these reactions it was of interest to study the effect of various substituents on the course of the telomerization.

The experiments showed that the reaction of equimolecular amounts of octamethylcyclotetrasiloxane and dichloromethylvinylsilane proceeded in accordance with the equation



A mixture of telomer-homologs was then formed; of these we isolated  $\alpha$ -chloro- $\alpha$ -methyl- $\alpha$ -vinyl  $\omega$ -chloro- $\omega$ , $\omega$ -dimethyl polysiloxanes for which  $n = 1, 2$ , and 3 and characterized them by their boiling points, refractive indices, specific gravities, molecular refractions, elementary analyses, and bromine values. The properties of the compounds isolated are given in Table 1, and the elementary analyses and bromine values are given in Table 4.

TABLE 1

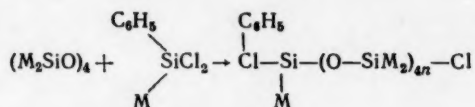
Formula	B.p. in °C (p in mm)	$d_4^{20}$	$n_D^{20}$	MR	
				Calc.	Found
$\begin{array}{c} \text{CH}=\text{CH} \quad \text{CH}_3 \\   \quad \quad   \\ \text{Cl}-\text{Si}-(\text{OSi})_n-\text{Cl} \\   \quad \quad   \\ \text{CH}_2 \quad \text{CH}_3 \end{array}$	107 (3)	1,0115	1,4153	108,44	108,24
$\begin{array}{c} \text{CH}_2=\text{CH} \quad \text{CH}_3 \\   \quad \quad   \\ \text{Cl}-\text{Si}-(\text{OSi})_n-\text{Cl} \\   \quad \quad   \\ \text{CH}_2 \quad \text{CH}_3 \end{array}$	197-199 (3)	0,9966	1,4121	183,02	183,29
$\begin{array}{c} \text{CH}_2=\text{CH} \quad \text{CH}_3 \\   \quad \quad   \\ \text{Cl}-\text{Si}-(\text{OSi})_{11}-\text{Cl} \\   \quad \quad   \\ \text{CH}_2 \quad \text{CH}_3 \end{array}$	255-257 (3)	0,9849	1,4086	259,01	258,31

TABLE 2.

Formula	B.p. in °C (p in mm)	$d_4^{20}$	$n_D^{20}$	MR	
				Calc.	Found
$\begin{array}{c} \text{C}_6\text{H}_5 \text{ CH}_3 \\   \quad   \\ \text{Cl}-\text{Si}-(\text{OSi})_4-\text{Cl} \\   \quad   \\ \text{CH}_3 \text{ CH}_3 \end{array}$	147—149 (3)	1,05232	1,4524	124,01	123,92
$\begin{array}{c} \text{C}_6\text{H}_5 \text{ CH}_3 \\   \quad   \\ \text{Cl}-\text{Si}-(\text{OSi})_4-\text{Cl} \\   \quad   \\ \text{CH}_3 \text{ CH}_3 \end{array}$	239—241 (3)	1,0483	1,4458	198,59	198,54

After several repeat experiments it was found that the average conversion of dichloromethylvinylsilane was 32.8% and that of octamethylcyclotetrasiloxane was 54.0%. The yield of telomers was 45.1% on the weight of the original mixture, and the contents of the individual telomer-homologs with  $\bar{n} = 1, 2$ , and 3 were 18.5%, 30.8%, and 14.6%, respectively. Higher telomers with a degree of polymerization of  $\bar{n} > 3$  were formed to the extent of 36.1%. Thus compounds of the  $\alpha$ -chloro- $\alpha$ -methyl- $\alpha$ -vinyl  $\omega$ -chloro- $\omega$ ,  $\omega$ -dimethyl polysiloxane series with given numbers of silicon atoms have been prepared by the telomerization reaction; this is as yet the only reaction by means of which the synthesis of such compounds has been effected.

The reaction between octamethylcyclotetrasiloxane and dichloromethylphenylsilane was carried out with the object of preparing telomer-homologs of the  $\alpha$ -chloro- $\alpha$ -methyl- $\alpha$ -phenyl  $\omega$ -chloro- $\omega$ ,  $\omega$ -dimethyl polysiloxane series. The first experiments showed that under standard conditions (250°, three hours) the conversion was very low (the total amount of telomers was less than 10% on the weight of the reactants taken). Further experiments were carried out at 300° for five hours with 2 moles of dichloromethylphenylsilane to each mole of octamethylcyclotetrasiloxane. However, even under these conditions the conversion was only 18.4%; the conversion of dichloromethylphenylsilane was 9.1% and that of octamethylcyclotetrasiloxane was 19.0%. From the reaction products



we isolated telomer-homologs with  $\bar{n} = 1$  and 2, and 49.0% of the total amount of telomers boiled above 350° (3 mm). The properties of 1, 9-dichlorononamethyl-9-phenylpentasiloxane and 1, 17-dichloroheptadecamethyl-17-phenylnonasiloxane are given in Table 2.

Hence, in the reaction of octamethylcyclotetrasiloxane with dichloromethylphenylsilane telomer-homologs of the  $\alpha$ -chloro- $\alpha$ -methyl- $\alpha$ -phenyl  $\omega$ -chloro- $\omega$ ,  $\omega$ -dimethyl polysiloxane series are formed.

#### EXPERIMENTAL

**Reaction of Octamethylcyclotetrasiloxane with Dichloromethylvinylsilane.** For the syntheses we used octamethylcyclotetrasiloxane of b.p. 174–176°, (mole. wt. 296.6) and dichloromethylvinylsilane of b.p. 93° (Cl 50.6%). An autoclave was charged with 148.0 g (0.5 mole) of octamethylcyclotetrasiloxane and 70.5 g (0.5 mole) of dichloromethylvinylsilane. The reaction procedure was similar to that for dichlorodimethylsilane [2]. The reaction products (215 g) were fractionated first through a column of 10-plate efficiency and then from a flask having a column. Data on the separation of the products are given in Table 3.

From fraction IV, after passage through the fractionation column, we isolated pure

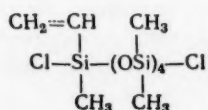


TABLE 3.

Frac- tion	B.p. of frac- tion in °C (p in mm)	Yield, g	Cl content, %	Content of products (g)					Resi- due
				CH=CH   SiCl <sub>2</sub>   CH <sub>3</sub>	[(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>n</sub> , Cl calc = 16.2	Si <sub>5</sub> Cl <sub>calc</sub> = 9.64	Si <sub>9</sub> Cl <sub>calc</sub> = 6.88	Si <sub>13</sub> Cl <sub>calc</sub> = 6.88	
I	up to 100	40,2	50,62	40,2					
II	100—185	74,3	4,29	7,2	67,1				
III	до 90 (3)	2,8	7,8		1,3	1,5			
IV	90—120 (3)	11,1	15,7			11,1			
V	120—185 (3)	20,5	11,5			5,7			
VI	185—205 (3)	8,4	9,62				14,8		
VII	205—245 (3)	14,6	8,15				8,4		
VIII	245—265 (3)	6,8	7,14				7,0	7,6	
IX	Residue	35,0	6,31					6,8	35,0
Total		213,7		47,2	68,4	18,3	30,2	14,4	35,0

\* Average value from two determinations.

TABLE 4.

n	B.p. in °C (p in mm)	C, %		H, %		Si, %		Cl, %		Bromine value	
		calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
1	107,3	30,19	29,95	6,9	6,75	32,06	32,65	16,2	16,1	36,6	35,2
			30,01		6,59		32,41		15,85		34,9
2	197—199 (3)	31,04	30,62	7,54	7,31	34,33	33,76	9,64	9,51	21,6	19,5
			30,82		7,40		33,80		9,09		20,3
3	255—257 (3)	31,47	31,18	7,63	7,25	35,37	35,43	6,88	6,43	15,0	11,5
			31,10		7,40		35,30		6,80		12,0

and from Fractions VI, and VIII, by two distillations from a flask with a column, we obtained pure

$$\text{Cl}-\text{Si}\begin{array}{c} \text{CH}_2=\text{CH} \\ | \\ \text{CH}_3 \end{array}-(\text{OSi})_8-\text{Cl}\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$

and

$$\text{Cl}-\text{Si}\begin{array}{c} \text{CH}_2=\text{CH} \\ | \\ \text{CH}_3 \end{array}-(\text{OSi})_{12}-\text{Cl}\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$

The elementary analyses and bromine values of the compounds isolated of general formula

$$\text{Cl}-\text{Si}\begin{array}{c} \text{CH}_2=\text{CH} \\ | \\ \text{CH}_3 \end{array}-\left(\text{OSi}\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}\right)_n-\text{Cl}$$

are given in Table 4.

**Reaction of Octamethylcyclotetrasiloxane with Dichloromethylphenylsilane.** The reaction of octamethylcyclotetrasiloxane with dichloromethylphenylsilane was carried out in an autoclave at 300° for five hours. We took 221.5 g (0.72 mole) of octamethylcyclotetrasiloxane and 266.5 g (1.44 moles) of dichloromethylphenylsilane, b.p. 200–202° (Cl 37.0%). From the autoclave we discharged 475 g of product, from which distillation up to 100° (10 mm) gave 390.6 g (Cl 24.8%) of unchanged reactants. From 83.94 g of still residue the first fractionation gave 43.4 g of volatile oligomers which came over up to 350° (3 mm), and the nondistilling residue amounted to 40.5 g. By repeated refraction-



ation of the fraction of b.p. up to 350° (3 mm) we obtained 6.6 g of pure  $\text{Cl}-\text{Si}-[\text{OSi}(\text{CH}_3)_2]_4$ . Found: C 37.48; 37.62; H 6.33; 6.35; Si 28.11; 28.33; Cl 15.00; 14.97%.  $\text{C}_{15}\text{H}_{32}\text{O}_4\text{Si}_5\text{Cl}_2$ . Calculated: C 36.91; H 6.60; Si 28.75;

$\text{Cl}-\text{Si}-[\text{OSi}(\text{CH}_3)_2]_3-\text{Cl}$ . Found: C 36.01; 35.81; H 6.98; 7.11; Si 31.97; 31.62; Cl 9.23; 9.14%;  $\text{C}_{23}\text{H}_{56}\text{O}_8\text{Si}_9\text{Cl}_2$ . Calculated: C 35.3; H 7.16; Si 32.2; Cl 9.66%.

#### SUMMARY

1. The reactions of octamethylcyclotetrasiloxane with dichloromethylvinylsilane and with dichloromethylphenylsilane proceed as teleomerization reactions.
2. Five telomer-homologs of two homologous series were isolated.
3. The telomerization of octamethylcyclotetrasiloxane with dichloromethylvinylsilane and with dichloromethylphenylsilane may serve as a method for the preparation of oligomers for the synthesis of polymers of regular structure.

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# REACTION OF TRIALKYL (OR ARYL) SILANOLS WITH (ETHOXYMETHYLSILYL) METHYL DIMETHYLPHOSPHINATES

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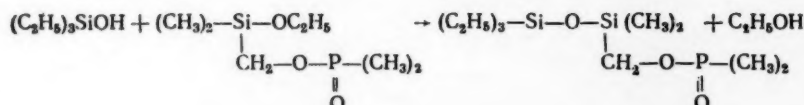
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 10, pp. 1792-1794, October, 1961

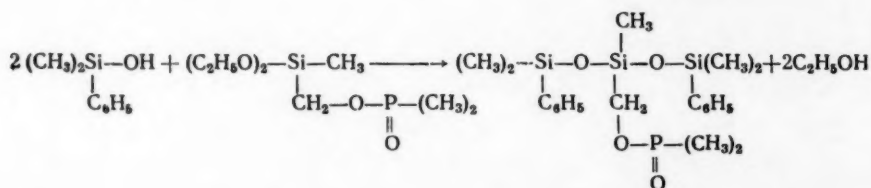
Original article submitted April 6, 1961

In Smith's papers it was shown that an ethoxy group attached to silicon in alkoxysilanes reacting with alkylsilanols in presence of sodium [1] or sodium alkoxide [2] as catalyst is replaced by an alkylsiloxy group. It was of interest to study the replacement of an alkoxy group in various organosilicon compounds containing dimethylphosphinic acid residues among their terminal groups. In carrying out the replacement of ethoxy groups attached to silicon by trialkyl (or aryl) siloxy groups, we have opened up great possibilities for the synthesis of new compounds containing two or more silicon atoms as well as phosphorus.

Investigation of the reaction of (ethoxydimethylsilyl) methyl dimethylphosphinate with triethylsilanol at a ratio of 1 : 1 showed that heating of the reaction mixture at 140-150° leads to the liberation of ethanol and the formation of (3, 3, 3-triethyl-1, 1-dimethyldisiloxanyl) methyl dimethylphosphinate in 60% yield in accordance with the scheme:



In the reaction of (ethoxydimethylsilyl) methyl dimethylphosphinate with dimethylphenylsilanol and with methyldiphenylsilanol we obtained, respectively, (1, 1, 2, 3-tetramethyl-3-phenyldisiloxanyl) methyl dimethylphosphinate. This reaction is of general significance; it occurs with the replacement not only of one, but also of two silicon-attached ethoxy groups. Thus, in the reaction of dimethylphenylsilanol with (diethoxymethylsilyl) methyl dimethylphosphinate at a ratio of 2 : 1 we obtained [1-(dimethylphenylsiloxy)-1, 3, 3-trimethyl-3-phenyldisiloxanyl] methyl dimethylphosphinate:



Analogous reactions were carried out with triethylsilanol and with methyldiphenylsilanol. In all cases the reactions were carried out without a catalyst. The ethanol formed in the reaction was distilled off in the course of the experiment and identified by its boiling point and refractive index. As a result of the reactions carried out we obtained previously undescribed organosilicon compounds containing two or three silicon atoms and a dimethylphosphinic acid group. The products are colorless liquids which may be distilled in a vacuum and are readily soluble in organic solvents. The properties of the products are presented in the table.

No.	Formula of substance	B.p. in °C (p in mm)	$n_D^{20}$	$d_4^{20}$	MR	
					Found	Calc.
I	$  \begin{array}{c}  (C_6H_5)_3Si-O-Si-(CH_3)_3 \\    \\  C-H_2-O-P(O)(CH_3)_2  \end{array}  $	117—118(2)	1,4409	0,9609	81,48	81,87
II	$  \begin{array}{c}  (CH_3)_2C_6H_5-Si-O-Si-CH_3 \\    \\  CH_2-O-P(O)(CH_3)_2  \end{array}  $	155—157(2)	1,4820	1,0329	87,40	88,10
III	$  \begin{array}{c}  CH_3(C_6H_5)_2-Si-O-Si-(CH_3)_2 \\    \\  CH_2-O-P(O)(CH_3)_2  \end{array}  $	172—174(0,15)	1,5275	1,0780	108,00	108,30
IV	$  \begin{array}{c}  (C_6H_5)_3Si-O-Si-O-Si-(C_6H_5)_3 \\    \qquad \qquad   \\  CH_2-O-P(O)(CH_3)_2  \end{array}  $	153—156(1—1,5)	1,4442	0,9634	114,20	114,58
V	$  \begin{array}{c}  CH_3 \quad CH_3 \quad CH_3 \\    \quad   \quad   \\  C_6H_5-Si-O-Si-O-Si-C_6H_5 \\    \quad   \quad   \\  CH_2 \quad CH_2 \quad CH_2 \\  \quad \quad   \\  \quad \quad O-P(O)(CH_3)_2  \end{array}  $	147—150(0,15)	1,5034	1,0615	126,40	126,90
VI	$  \begin{array}{c}  CH_3 \quad CH_3 \quad C_6H_5 \\    \quad   \quad   \\  C_6H_5-Si-O-Si-O-Si-CH_3 \\    \quad   \quad   \\  C_6H_5 \quad CH_2-O-P(O)(CH_3)_2  \end{array}  $	250(1·10 <sup>-4</sup> )	1,5580	1,1178	166,5	167,2

## EXPERIMENTAL

Dimethylphenylsilanol and methyldiphenylsilanol were prepared by the method of Andrianov and Delazari [3]. The preparation of (ethoxydimethylsilyl) methyl dimethylphosphinate and (diethoxymethylsilyl) methyl dimethylphosphinate were described by us in a previous communication [4].

**Synthesis of (3, 3,3-Triethyl-1, 1-dimethyldisiloxanyl) methyl Dimethylphosphinate (I).** A mixture of 4.2 g (0.02 mole) of (ethoxydimethylsilyl) methyl dimethylphosphinate and 2.65 g (0.02 mole) of triethylsilanol was prepared in a Claisen flask fitted with thermometer, stirrer, and condenser with receiver set for distillation. With vigorous stirring the reaction mixture was heated at 140–150° for 4.5 hours. In the course of the experiment 0.7 g (75%) of alcohol, b.p. 78° and  $n_D^{20}$  1.3625, was distilled off. The residue was vacuum fractionated. We obtained 3.5 g (60%) of product; b.p. 117–118° (2 mm);  $n_D^{20}$  1.4409;  $d_4^{20}$  0.9609; found MR 81.48; calculated MR 81.87. Found: C 44.55; H 9.89%.  $C_{11}H_{20}O_3PSi_2$ . Calculated: C 44.55; H 9.86%.

**Synthesis of (1, 1, 3, 3-Tetramethyl-3-phenyldisiloxanyl) methyl Dimethylphosphinate (II).** Similarly, from 4.21 g (0.02 mole) of (ethoxydimethylsilyl) methyl dimethylphosphinate and 3.05 g (0.05 mole) of dimethylphenylsilanol we obtained 20 g (about 30%) of product; b.p. 155–157° (2 mm);  $n_D^{20}$  1.4820;  $d_4^{20}$  1.0329; found MR 87.37; calculated MR 88.13. Found: C 48.9; H 7.94; Si 17.9%.  $C_{13}H_{25}O_3PSi_2$ . Calculated: C 49, 3; H 7.96; Si 17.8%.

**Synthesis of (1, 1, 3-Trimethyl-3, 3-diphenyldisiloxanyl) methyl Dimethylphosphinate (III).** From 4.21 g (0.02 mole) of (ethoxydimethylsilyl) methyl dimethylphosphinate and 4.28 g (0.02 mole) of methyldiphenylsilanol we obtained 5 g (65%) of product; b.p. 172–174° (0.15 mm);  $n_D^{20}$  1.5275;  $d_4^{20}$  1.0780; found MR 108.0; calculated MR 108.3. Found C 57.09; H 7.4; ash 50.49%.  $C_{18}H_{27}O_3PSi_2$ . Calculated: 57.10; H 7.2; ash 50.63%.

**Synthesis of [3, 3, 3-Triethyl-1-methyl-1-(triethylsiloxy) disiloxanyl] methyl Dimethylphosphinate (IV).** Similarly, on heating 7.2 g (0.03 mole) of (diethoxymethylsilyl) methyl dimethylphosphinate with 7.95 g (0.06 mole) of triethylsilanol at 140–150° for five hours, we distilled off 2.7 g (75%) of ethanol. On fractionation of the residue we collected a fraction of b.p. 153–156° (1–1.5 mm); yield 7.6 g (70%);  $n_D^{20}$  1.4442;  $d_4^{20}$  0.9634; found MR 114.2; calculated MR 114.58. Found: C 46.69; H 10.07; Si 20.5%; mol. wt. 413.0.  $C_{16}H_{41}O_4PSi_3$ . Calculated: C 46.60; H 10.01; Si 20.4%; mol. wt. 413.0.

Synthesis of [1-(Dimethylphenylsiloxy)-1, 3, 3-trimethyl-3-phenyldisiloxanyl] methyl Dimethylphosphinate

(V). Similarly, from 7.2 g (0.03 mole) of (diethoxymethylsilyl) methyl dimethylphosphinate and 9.15 g (0.06 mole) of dimethylphenylsilanol we obtained 8.0 g (60%) of product; b.p. 147-150° (0.15 mm);  $n_D^{20}$  1.5034;  $d_4^{20}$  1.0615; found MR 126.4; calculated MR 126.9. Found: C 53.41; H 7.50; S 18.72%.  $C_{20}H_{33}O_4PSi_3$ . Calculated: C 53.1; H 7.40; S 18.63%.

Synthesis of [1, 2-Dimethyl-1-(methyldiphenylsiloxy)-3, 3-diphenyl-disiloxanyl] methyl Dimethylphosphinate

(VI). Similarly, from 2.4 g (0.01 mole) of (diethoxymethylsilyl) methyl dimethylphosphinate and 4.28 g (0.02 mole) of methyldiphenylsilanol we obtained 1.8 g (30%) of product; b.p. 250° ( $1 \cdot 10^{-4}$  mm);  $n_D^{20}$  1.5580;  $d_4^{20}$  1.1178; found MR 166.5; calculated MR 167.2. Found: C 62.3; H 6.50; Si 14.20; ash 43.33%.  $C_{30}H_{37}O_4PSi_3$ . Calculated: C 62.4; H 6.50; Si 14.61; ash 43.55%.

SUMMARY

1. An investigation was made of the reaction of trialkyl (or aryl) silanols with (ethoxymethylsilyl) methyl dimethylphosphinates; it can serve as a method of synthesizing organosilicon compounds containing the dimethylphosphinic acid group.

2. New compounds containing phosphorus and two or more silicon atoms were synthesized and characterized.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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REARRANGEMENT OCCURRING IN THE DEHYDROCHLORINATION  
OF 1, 1-AND 1, 2-BISTRICHLOROSILYL-1, 2-DICHLOROETHANES  
WITH ALUMINUM CHLORIDE

V. F. Mironov and V. V. Nepomnina

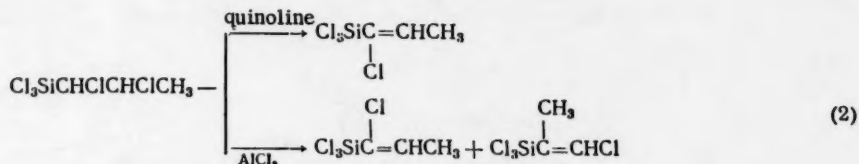
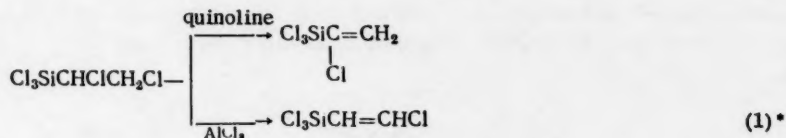
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*.

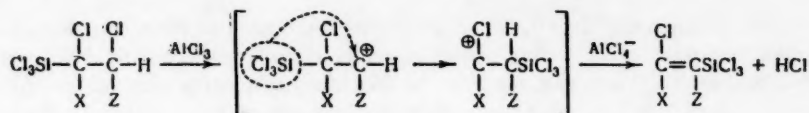
No. 10, pp. 1795-1799, October, 1961

Original article submitted May 10, 1961

In previous investigations [1, 2] it was shown that, depending on the dehydrochlorinating agent used, the elimination of hydrogen chloride from certain trichloro-(1,2-dichloroalkyl) silanes leads to different unsaturated compounds:



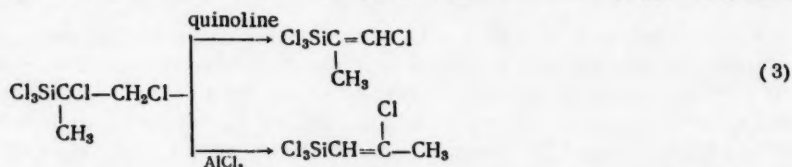
On the basis of these results it was suggested [6] that the rearrangement of these compounds in the course of their dehydrochlorination with aluminum chloride proceeds through the stage of the isomerization of an intermediate  $\beta$ -carbenium ion.



in which X and Z = H and H; H and CH<sub>3</sub>

Scheme 1

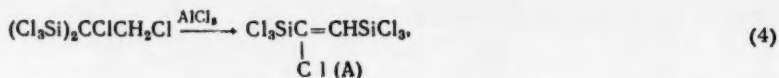
We later confirmed the probability of this mechanism in an investigation of the dehydrochlorination of trichloro-(2-dichloro-1-methylethyl)silane [7]. In this case ( $X = CH_3$ ,  $Z = H$ ), in full agreement with Scheme 1, the  $SiCl_3$  group moved from the  $\alpha$ -carbon to the  $\beta$ -carbon, which led to the complete isomerization of isopropyl into propenyl.



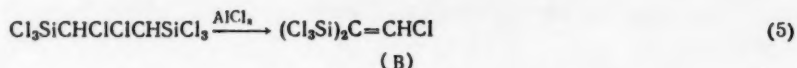
\*Analogous results were obtained in the dehydrohalogenation of  $\text{Cl}_3\text{SiCHBrCH}_2\text{Br}$  and  $\text{Cl}_3\text{GeCHClCH}_2\text{Cl}$  [3-5].



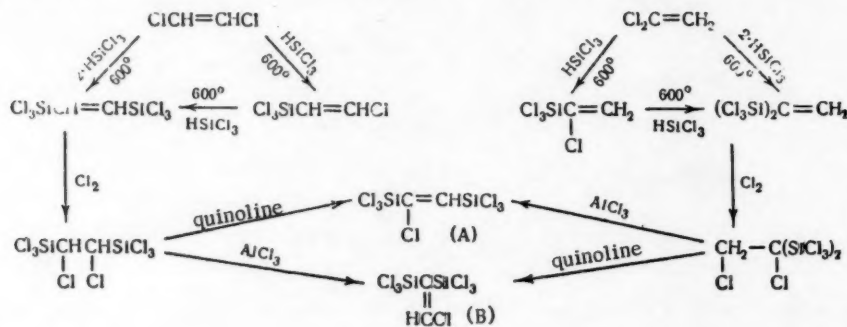
In the present work we decided to check the correctness of Scheme 1 in other cases. For this we investigated the dehydrochlorination of 1,1- and 1,2-bistrichlorosilyl-1,2-dichloroethanes with aluminum chloride. The dehydrochlorination of the first compound ( $X = \text{SiCl}_3$ ;  $Z = \text{H}$ ) in accordance with Scheme 1 should lead to chloro-1,1-bistrichlorosilylethylene (A).



whereas the dehydrochlorination of the second compound ( $X = \text{H}$ ;  $Z = \text{SiCl}_3$ ) should lead to chloro-1,1-bistrichlorosilylethylene (B).



The structures of the compounds obtained in accordance with Equations (4) and (5) were found to be those expected; this was proved by confirmatory syntheses of these compounds (Scheme 2). Hence, our view that in the dehydrochlorination of (1,2-dichloroalkyl)silanes with aluminum chloride there occurs isomerization of the intermediate unstable particle (most likely a  $\beta$ -carbenium ion) becomes still more probable.



Scheme 2

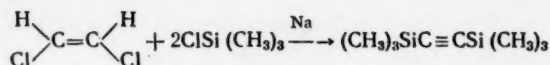
The synthesis of the starting compounds by the method of high-temperature condensation is of interest on its own account [8, 9]. The investigation of the high-temperature reaction of silanes containing silicon-attached hydrogen with various chloro olefins in a flow system led us to the conclusion that this process not only forms a new general method for the preparation of unsaturated organosilicon compounds, but is a fundamentally new method of forming an Si-C bond proceeding by a homolytic-substitution mechanism [8, 9]



in which R is an unsaturated group.

In the development of this method we have now carried out the high-temperature condensation of  $\text{HSiCl}_3$  with 1,2-dichloroethylenes and with vinylidene chloride, and also with (1- and 2-chlorovinyl)trichloro-silanes (see Scheme 2). It is interesting that irrespective of whether cis- or trans-dichloroethylene is used in this reaction the product, formed with the same yield (about 40%) in each case, was 1,2-bistrichlorosilylethylene, m.p.  $36^\circ$ , with a little bistrichlorosilylacetylene. We obtained a somewhat better yield of  $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$  (about 60%) when trichloro-(2-chlorovinyl)silane was used in the condensation with  $\text{HSiCl}_3$ .

The properties of  $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$  prepared by high-temperature condensation were completely identical with those of the 1,2-bistrichlorosilylethylene synthesized in other ways and proved on the basis of its Raman and infrared spectra, and also dipole moment measurements, to have the trans-configuration [10-13]. Our attempts to prepare  $(\text{CH}_3)_3\text{SiCH}=\text{CHSi}(\text{CH}_3)_3$  in the cis-form by organosodium synthesis from cis-dichloroethylene were unsuccessful; only bistrimethylsilylacetylene was obtained:



The high-temperature condensation of  $\text{HSiCl}_3$  with vinylidene chloride gave a low yield (8%) of 1,1-bistrichlorosilylethylene. Only by the use of trichloro(1-chlorovinyl)silane in condensation with  $\text{HSiCl}_3$  did we succeed in raising the yield of  $(\text{Cl}_3\text{Si})_2\text{C}=\text{CH}_2$  to 20% (see Scheme 2). In both cases the  $(\text{Cl}_3\text{Si})_2\text{C}=\text{CH}_2$  obtained contained 5-8% of  $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$ , and also a considerable amount (up to 40%) of aromatic compounds, among which we identified trichlorophenylsilane. After the addition of chlorine to  $(\text{Cl}_3\text{Si})_2\text{C}=\text{CH}_2$  trichlorophenylsilane could easily be removed by distillation.

## EXPERIMENTAL

**1,2-Bistrichlorosilylethylene  $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$ .** A. A mixture of 194 g of trans-dichloroethylene and 650 g of trichlorosilane was passed in the course of 26 hours 15 minutes through an empty silica tube (100 mm, diameter 15 mm) heated to  $650 \pm 10^\circ$  in a tube furnace. The rate of passage was 32.5 g/hour (one drop per second), and the time of contact was 34 seconds. By fractionation through a column we isolated: 1) 100 g of  $\text{HSiCl}_3$ , b.p. 31-32°; 2) 130 g of  $\text{SiCl}_4$ , b.p. 56-57°; 3) 50 g of  $\text{Cl}_3\text{SiCH}=\text{CH}_2$ , b.p. 91-92°; 4) 215 g (37%) of  $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$ , b.p. 190-192°. The melting point of the resulting  $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$  was raised to 36° after repeated decantation of the liquid part from the crystals; the liquid part obtained, m.p. 5-15°, amount to 8 g. The Raman and infrared spectra of this liquid showed that the main lines belonged to the trans form of  $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$ , the lines 999 and 1033  $\text{cm}^{-1}$  belonged to an aromatic compound, and the line at 2145  $\text{cm}^{-1}$  could indicate the presence of a triple bond. We therefore carried out the methylation ( $\text{CH}_3\text{MgCl}$ ) of this liquid and as a result obtained a substance of b.p. 141-143°, which, according to the Raman and infrared spectra, contained trans- $(\text{CH}_3)_3\text{SiCH}=\text{CHSi}(\text{CH}_3)_3$  and  $(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3$ , the latter being in the predominant amount.

B. Under strictly analogous conditions we carried out the condensation of 179 g of cis-dichloroethylene and 600 g of trichlorosilane. The yields and relative amounts of the substances formed were found to be identical with those obtained in Experiment A. Methylation of the  $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$  obtained in this experiment with methylmagnesium chloride gave a 72% yield of  $(\text{CH}_3)_3\text{SiCH}=\text{CHSi}(\text{CH}_3)_3$ , and the Raman and infrared spectra of this were in full agreement with those published earlier [10] for the trans-isomer.

C. Condensation under analogous conditions of 150 g of  $\text{Cl}_3\text{SiH}$  with 190 g of  $\text{Cl}_3\text{SiCH}=\text{CHCl}$  led to 180 g (61%) of  $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$ .

**1,1-Bistrichlorosilylethylene  $(\text{Cl}_3\text{Si})_2\text{C}=\text{CH}_2$ .** A. Condensation under the above-described conditions of 374 g of  $\text{HSiCl}_3$  with 266 g of  $\text{CH}_2=\text{CCl}_2$  led to: 1) 35 g (16%) of  $\text{Cl}_3\text{SiCH}=\text{CH}_2$ , b.p. 91-92°; 2) 15 g (3%) of  $\text{Cl}_3\text{SiCCl}=\text{CH}_2$ , b.p. 123°; 3) 34 g (5%) of a fraction of b.p. 190-195°, which according to the Raman and infrared spectra correspond to the analogous fractions in Experiments B and C.

B. Condensation of 748 g of  $\text{HSiCl}_3$  with 266 g of  $\text{CH}_2=\text{CCl}_2$  led to a fraction, b.p. 190-195°, amounting to 45 g (8%).

C. By the condensation of 190 g of  $\text{Cl}_3\text{SiCCl}=\text{CH}_2$  with 150 g of  $\text{HSiCl}_3$  we obtained: 1) 50 g of  $\text{HSiCl}_3$ , b.p. 31-32°; 2) 103 g of  $\text{SiCl}_4$ , b.p. 56-57°; 3) 38 g of  $\text{Cl}_3\text{SiCH}=\text{CH}_2$ , b.p. 91-92°; 4) 5 g (20%) of  $(\text{Cl}_3\text{Si})_2\text{C}=\text{CH}_2$ ; b.p. 192-195°;  $n_D^{20}$  1.4931;  $d_4^{20}$  1.4987; found MR 57.2; calculated MR 55.74. The lines 999 (4 sh), 1032, 1593  $\text{cm}^{-1}$  in the Raman spectrum of this compound indicated that it contained up to 40% of aromatic compounds. Methylation of the resulting  $(\text{Cl}_3\text{Si})_2\text{C}=\text{CH}_2$  led to a substance whose Raman spectrum showed the presence of  $(\text{CH}_3)_3\text{Si}_2\text{C}=\text{CH}_2$  and up to 10% of  $(\text{CH}_3)_3\text{SiCH}=\text{CHSi}(\text{CH}_3)_3$ . In addition, weak lines belonging to  $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_3$  were noted.

**Dichloro-1,2-bistrichlorosilylethane  $\text{Cl}_3\text{SiCHClClCHSiCl}_3$ .** Through 121 g of  $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$  we passed chlorine until the weight had increased by the required amount, which took eight hours. Vacuum distillation gave 119 g (79.3%) of  $\text{Cl}_3\text{SiCHClClCHSiCl}_3$ ; b.p. 86-86.5° (3 mm);  $n_D^{20}$  1.5116;  $d_4^{20}$  1.6772; found MR 65.5; calculated MR 65.8.

Dichloro-1,1-bistrichlorosilylethane  $(\text{Cl}_3\text{Si})_2\text{CClCH}_2\text{Cl}$ . Passage of chlorine through 74 g of  $(\text{Cl}_3\text{Si})_2\text{C}=\text{CH}_2$  led to only one-half of the theoretical increase in weight. Vacuum distillation gave 38 g (40.4%) of  $(\text{Cl}_3\text{Si})_2\text{CClCH}_2\text{Cl}$ ; b.p. 93-94° (3 mm);  $n_D^{20}$  1.5160. In addition we isolated 20 g of a fraction of b.p. 56-57° (3 mm), whose Raman spectrum corresponded to  $\text{C}_6\text{H}_5\text{SiCl}_3$ . Methylation  $(\text{CH}_3\text{MgCl})$  of this fraction gave a 33% yield of  $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_3$ , whose spectrum coincided completely with that of the standard sample of this substance.



Dehydrochlorination of  $\text{Cl}_3\text{SiCHClCHSiCl}_3$ . A. A mixture of 69 g of  $\text{Cl}_3\text{SiCHClCHSiCl}_3$  and 3.5 g of piperidine was slowly distilled under a vacuum of 130-150 mm from a 200-ml flask. Redistillation of the condensate gave 47 g (75.8%) of chloro-1,2-bistrichlorosilylethylene (A); b.p. 63-63.3° (3 mm); m.p. 0-15°;  $n_D^{20}$  1.5020;  $d_4^{20}$  1.5923; found MR 61.04; calculated MR 60.6; yield 75.8%.

Raman spectrum ( $\Delta\nu$ ,  $\text{cm}^{-1}$ ): 173 (3), 203 (1), 298 (2), 332 (10), 488 (2), 519 (10), 594-613 (v.b.), 809 (0), 920 (1b), 1001 (0), 1037 (1b), 1109 (1b), 1221 (4b), 1576 (10), 2878 (2b), 3001 (4b).

B. A mixture of 38 g of  $\text{Cl}_3\text{SiCHClCHSiCl}_3$  and 0.5 g of aluminum chloride was distilled slowly at atmospheric pressure; toward the end of the distillation a vacuum was applied, and the contents of the flask were distilled to dryness. Redistillation gave 18 g (55%) of chloro-1,1-bistrichlorosilylethylene (B); b.p. 63-64° (3 mm); m.p. from -15° to -11°;  $n_D^{20}$  1.5083;  $d_4^{20}$  1.6214; found MR 60.5; calculated MR 60.6.

Raman spectrum ( $\Delta\nu$ ,  $\text{cm}^{-1}$ ): 184 (4), 198 (5), 222 (6), 255 (3), 293 (0), 330 (10), 446 (8), 495 (6), 519 (2), 583 (2b), 599 (2b), 802 (1b), 880 (1b), 962 (0), 1217 (1b), 1315 (4), 1523 (9), 1573 (2), 2876 (2b), 3062 (2).

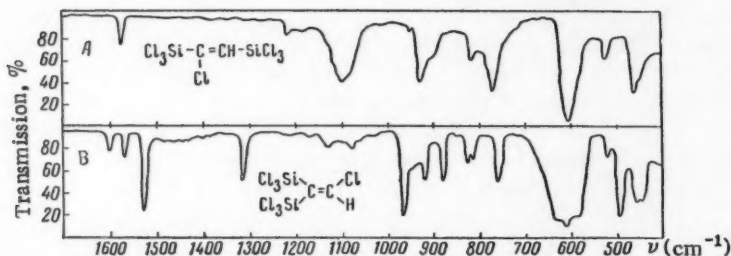


Fig. 1.

Dehydrochlorination of  $(\text{Cl}_3\text{Si})_2\text{CClCH}_2\text{Cl}$ . A. A mixture of 38 g of  $(\text{Cl}_3\text{Si})_2\text{CClCH}_2\text{Cl}$  and 0.5 g of aluminum chloride was distilled slowly at atmospheric pressure. Redistillation of the condensate gave 22 g (60%) of a fraction of b.p. 75-78° (6 mm) and  $n_D^{20}$  1.5030. Investigation of the Raman and infrared spectra of this fraction showed that it consisted of about 90% of chloro-1,2-bistrichlorosilylethylene (A), less than 10% of chloro-1,1-bistrichlorosilylethylene, and some aromatic compounds [lines in Raman spectrum: 1006 (5sh), 1039 (2), 1602 (4sh), and others].

B. A mixture of 18 g of  $(\text{Cl}_3\text{Si})_2\text{CClCH}_2\text{Cl}$  and 0.9 g of piperidine was distilled at 100 mm. By redistillation we isolated 6 g (40%) of a fraction of b.p. 65-70° (3 mm) and  $n_D^{20}$  1.5070. The infrared spectrum of this fraction coincided completely with that of  $(\text{Cl}_3\text{Si})_2\text{C}=\text{CHCl}$  (B).

Bis(trimethylsilyl)acetylene  $(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3$ . Sodium (34 g) was rapidly comminuted to a dust in 150 ml of boiling toluene by the use of a rapidly rotating stirrer. When cool, the toluene was poured off and replaced by 250 ml of ether. We then added 90 g of  $(\text{CH}_3)_3\text{SiCl}$ , 5 ml of cis-dichloroethylene, and 2 ml of ethyl acetate. When reaction had set in, the rest of the cis-dichloroethylene (in all 38 g) was added at such a rate that the ether boiled gently. The contents of the flask were boiled for ten hours and then filtered from salt, which was washed with fresh ether. Distillation through a column gave 15 g of  $(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3$ ; m.p. 133-5°, b.p. 21.8-22°;  $n_D^{25}$  1.4255;  $d_4^{25}$  0.7601; found MR 57.25; calculated MR 56.82. M.p. 133-135°;  $n_D^{25}$  1.4259;  $d_4^{25}$  0.763. Found: C 56.40; 56.50; H 10.67; 10.60; Si 32.70; 32.75%.  $\text{C}_8\text{H}_{18}\text{Si}_2$ . Calculated: C 56.41; H 10.60; Si 32.98%.

The Raman spectrum ( $\Delta\nu$ ,  $\text{cm}^{-1}$ ): 179 (5b), 218 (4v.b.), 306 (0), 340 (0), 406 (3b), 534 (0), 639 (8), 700 (4), 760 (3), 844 (2), 1132 (0), 1200 (0), 1257 (3b), 1323 (0), 1384 (0), 1417 (2b), 2114 (10), 2307 (10), 2968 (9).

The Raman and infrared spectra were determined by L. A. Leites.

## SUMMARY

1. On the basis of some new examples, the mechanism of the isomerization of ( $\alpha, \beta$ -dichloroalkyl)silanes in the course of their dehydrochlorination with aluminum chloride was confirmed.

2. By the high-temperature condensation of  $\text{HSiCl}_3$  with dichloroethylenes or with trichloro(1- and 2-chloro-vinyl)silanes, 1,1- and 1,2 bistrichlorosilylethylenes were prepared.

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# SYNTHESIS OF SURFACE-ACTIVE SUBSTANCES FROM $\omega$ -CHLORO CARBOXYLIC ACIDS

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Nesmeyanov and Freidlina with co-workers [1-6] showed that the  $\text{CCl}_3$  group of  $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes which they obtained by the telomerization of ethylene with carbon tetrachloride is hydrolyzed by sulfuric or nitric acid with formation of normal  $\omega$ -chloro carboxylic acids having chains of odd numbers of carbon atoms. From some  $\omega$ -chloro carboxylic acids (9-chlorononanoic, 11-chloroundecanoic, and 13-chlorotridecanoic acids) we have synthesized some surface-active substances of different types: anionic, cationic, and nonionic. As Rebinder and Taubman showed [7-9], one condition for high surface activity in organic substances is an optimum balance in the characters of the hydrophobic and hydrophilic parts of the molecule.

To increase the length of the hydrocarbon chain and change the physical and chemical properties, in particular to remove the dipolarity of the  $\omega$ -chloro carboxylic acid, the halogen was replaced by an aromatic group (phenyl\*, tolyl, naphthyl, phenoxy). This replacement was effected by alkylating the corresponding aromatic compound with the  $\omega$ -chloro carboxylic acids by the Friedel-Crafts method. As a result we obtained the following aryl carboxylic acids: 9-phenylnonanoic, 9-tolylnonanoic, 9-naphthylnonanoic, 9-phenoxyundecanoic, 11-phenylundecanoic, 11-tolylundecanoic, 11-phenoxyundecanoic, and 13-phenyltridecanoic. The characteristics of these are given in Table 1.

TABLE 1.

Acid	M.p.	B.p. in °C (p in mm)	$d_4^{20}$	$n_D^{20}$	C, %		H, %	
					found	calc.	found	calc.
9-Phenylnonanoic		177-179 (3)	0,993	1,5030	76,58	76,90	9,44	9,43
9-Phenoxyundecanoic	67-68	195-197 (3)	—	—	71,72	71,93	8,75	8,86
9-Naphthylnonanoic	—	222-225 (3)	—	—	79,78	80,24	8,57	8,51
11-Phenylundecanoic	—	191-193 (3)	0,976	1,4985	76,86	77,84	9,88	9,98
11-Phenoxyundecanoic	72-73	217-222 (3)	—	—	72,81	73,36	9,44	9,42
13-Phenyltridecanoic		205-211 (3)	—	—				
11-Tolylundecanoic		204-208 (4)	0,973	1,5012	78,64	78,21	10,28	10,21
9-Tolylnonanoic		194-198 (4)	0,989	1,5038	77,85	77,38	9,80	9,74

It should be noted that the replacement of chlorine in  $\omega$ -chloro carboxylic acids by aryl (phenyl, tolyl, naphthyl) results in the acid becoming a liquid at room temperature (m.p. below 0°). These acids have the advantage over unsaturated fatty acids in that they are stable to keeping. It is known that in most cases surface-active substances pre-

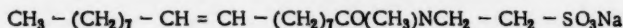
\* A benzene ring included in the straight chain of the hydrophobic part of a surface-active substance is equivalent to the lengthening of this chain by four carbon atoms.



pared from liquid acids have better technological properties than those derived from higher-melting acids (40-60°) for a given length of hydrophobic chain.

# EXPERIMENTAL

By condensing the acid chlorides of the above acids with taurines we obtained some anionic surface-active substances that differed among themselves only in the structure and composition of the hydrophobic part, which made it possible to determine the effect of the structure of the acid on the surface-activity properties of the product. To compare the physicochemical properties of the products we took the sodium salt of N-methyl-N-oleoyltaurine, which is widely used here and abroad under the trade name "Igepon T"; it has the formula:



The right-hand hydrophilic part of the substances synthesized (residue of N-methyltaurine sodium salt) remained unchanged in the first group of syntheses. The above-indicated aryl carboxylic acids were converted by the action of a 5-6 fold amount of thionyl chloride into their acid chlorides, which were condensed with the sodium salt of N-methyltaurine in a weakly alkaline medium with formation of the N-(arylalkanoyl)-N-methyltaurine sodium salt:

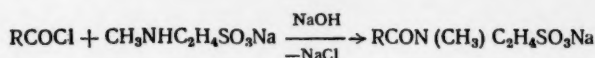


TABLE 2.

Surface-active substance *	Surface tension (erg/sq. cm)		Foam values (cc from 10 cc of soln.)						Crit. concn. for micelle formation (moles/liter)
	1% soln.	0.1% soln.	1% soln.			0.1% soln.			
			0	30 sec	3 min	0	30 sec	3 min	
N-Methyl-N-(9-phenylnonanoyl) taurine Na salt	35.6	-	450	200	0	-	-	-	$1.8 \cdot 10^{-3}$
N-Methyl-N-(11-phenylundecanoyl) taurine Na Salt	34.5	38.0	500	500	200	500	250	0	$1.3 \cdot 10^{-3}$
N-Methyl-N-(13-phenyltridecanoyl) taurine Na salt	32.8	-	620	620	600	550	550	550	-
N-Methyl-N-(9-phenoxynonanoyl) taurine Na salt	44.8	48.4	380	200	0	250	50	0	$1.3 \cdot 10^{-3}$
N-Methyl-N-(11-phenoxyun- decanoyl) taurine Na salt	44.2	47.2	350	250	0	300	50	0	$1.2 \cdot 10^{-3}$
N-Methyl-N-(9-naphthylnonanoyl) taurine Na salt	37.7	-	400	250	0	400	250	0	$1.4 \cdot 10^{-3}$
N-Methyl-N-(9-tolylundecanoyl) taurine Na salt	32.9	-	500	350	250	-	-	-	-
N-Methyl-N-(11-tolyundecanoyl) taurine Na salt	33.0	37.7	520	500	200	480	200	0	$1.4 \cdot 10^{-3}$
N-Methyl-N-oleoyltaurine Na salt (for comparison)	32.2	35.4	600	600	600	450	450	450	$1.2 \cdot 10^{-3}$

\*All determinations were carried out at pH 7.

As a result we obtained the anionic surface-active preparations listed in Table 2, from which it will be seen that with increase in the length of the chain in the hydrophobic part of the molecule the surface-activity properties of the substance improve and attain the level of the standard (N-methyl-N-oleoyltaurine sodium salt) at N-methyl-N-(13-phenyltridecanoyl)taurine sodium salt. The sodium salts of N-methyl-N-(11-tolylundecanoyl)taurine and of N-methyl-N-(11-phenylundecanoyl)taurine were close in properties to Igepon T. The introduction of an electro-negative element (e.g., oxygen in the phenoxy carboxylic acid) in the hydrophobic chain, as would be expected,

TABLE 3.

Surface-active substance	Surface tension (erg/sq. cm)		Foam values (cc from 10 cc of soln.)						Crit. concn. for micelle formation (moles/liter)
	1% soln.	0.1% soln.	1% soln.			0.1% soln.			
N-Methyl-N-(9-phenylnonanoyl) taurine Na salt	35.6	-	450	200	0	-	-	-	$1.8 \cdot 10^{-3}$
N-(9-Phenylnonanoyl) taurine Na salt	34.2	-	470	450	0	-	-	-	$1.9 \cdot 10^{-3}$
N-Methyl-N-(11-phenylundecanoyl) taurine Na salt	34.6	38.0	500	500	200	500	250	0	$1.3 \cdot 10^{-3}$
N-(11-Phenylundecanoyl) taurine Na salt	33.6	37.3	550	550	350	550	550	100	-

greatly reduces the surface activity of the substance, which may be explained by the reduction in the hydrophobic character of the chain due to the presence of the ether oxygen, which is capable of forming hydrogen bonds in an aqueous solution.

The lowering of the stability of the foam, i.e., of the elastoviscous properties of the adsorption film on introduction of the naphthyl group at the end of the hydrocarbon chain of the saturated aliphatic acid may be explained by the large transverse size of the naphthalene nucleus, which probably hinders the compact packing of the unimolecular adsorption layer at the interface of the phases. The investigation showed also that the products obtained do not lose their surface activity either in alkaline or in acid media; they are good dispersing agents for calcium soaps and are stable toward calcium and magnesium salts, i.e., may be used in hard water and in sea water, which is particularly valuable for many technological processes. The critical concentration for micelle formation is an important index of the properties of surface-active substance in various processes (emulsification, dispersion, solubilization, detergency, etc.). The fairly low values of the critical concentrations for micelle formation ( $c_{crit}$  was determined by the electrical conductivity method) in the synthesized products indicate their great tendency for micelle formation and consequently the possibility of utilizing them in the above-indicated technological processes.

To determine the effect of the structure and composition of the hydrophilic part on the surface-activity properties of the same preparations we synthesized two further substances, in which, unlike the first group of syntheses, only the hydrophilic part was changed. In this case, instead of N-methyltaurine sodium salt, we took the sodium salt of taurine itself. The results of the investigation are given in Table 3.

The replacement of the methyl group in N-methyltaurine by hydrogen for a given hydrophobic end of the molecule has a favorable effect on the surface activity, as can be seen from Table 3. This may be explained by the high mobility of the hydrogen of the amide group and the formation of the enol form of the carbonyl, which increases the hydrophilic properties of the taurides.

#### SUMMARY

1. A series of anionic surface-active substances, namely N- $\omega$ -arylalkanoyl-N-methyltaurines, were prepared from aryl carboxylic acids.
2. The relation was shown of the surface activities of the substances to their chemical structures, mainly the structures of the hydrophobic parts of the molecules: the length of the alkyl chain ( $C_9 - C_{13}$ ), the structure of the aryl group (phenyl, naphthyl), the effect of the presence of ether oxygen.
3. In hydrophobic character the hydrocarbon groups of 13-phenyltridecanoic and of 11-tolylundecanoic acids are equivalent to that of oleic acid and may replace it in the manufacture of surface-active substances.

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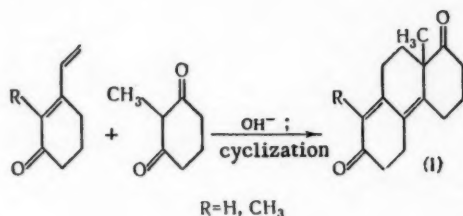
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SYNTHESIS OF 4,6,7,8-TETRAHYDRO-5-VINYL-2(3H)-  
NAPHTHALENONE AND ITS CONDENSATION WITH 2-METHYL-  
1,3-CYCLOHEXANEDIONE TO GIVE 14 $\xi$ -HYDROXY-D-HOMO-  
19-NORANDROSTA-4,9(10)-DIENE-3,17a-DIONE

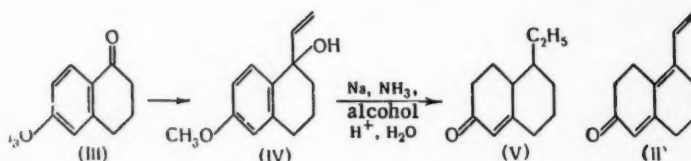
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,  
No. 10, pp. 1803-1810, October 1961  
Original article submitted March 30, 1961

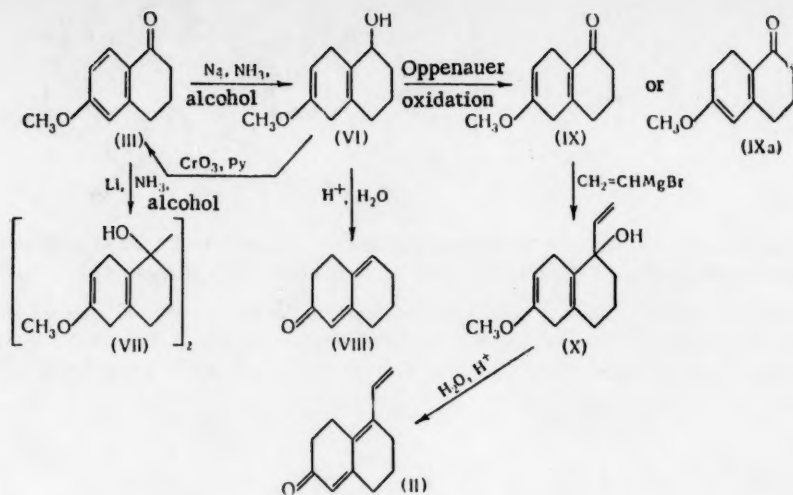
In a previous communication [1] it was shown that the monocyclic conjugated dienones 3-vinyl-2-cyclohexen-1-one and 2-methyl-3-vinyl-2-cyclohexen-1-one, when submitted to Michael condensation with 2-methyl-1,3-cyclohexanedione with subsequent cyclization, form tricyclic diketones of the type (I), which it was proposed to apply in the synthesis of D-homo steroids



However, numerous attempts to "graft" an A ring in the diketones (I) were unsatisfactory. In this connection the idea arose of synthesizing a bicyclic analog of the vinylcyclohexenones, namely 4,6,7,8-tetrahydro-5-vinyl-2(3H)-naphthalenone (II), which, in accordance with the scheme cited above would give directly a tetracyclic steroid diketone. As starting compound we used the accessible 3,4-dihydro-6-methoxy-1(2H)-naphthalenone (III), which it was proposed to convert into the known ethylenic alcohol (IV) and to reduce the latter by Birch's method to give (after hydrolysis) the desired trienone (II)



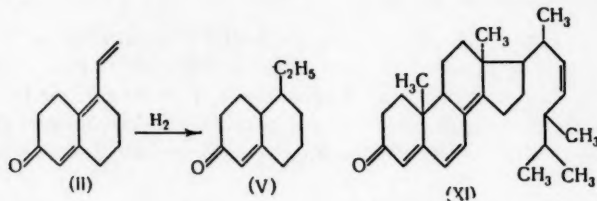
Actually, on reduction of the alcohol (IV) not only the aromatic ring was attacked, but also the vinyl and hydroxy groups, and from the reaction products we succeeded in isolating only 5-ethyl-4,4a,5,6,7,8-hexahydro-2(3H)-naphthalenone (V). For this reason we chose and carried out the following scheme:



3,4-Dihydro-6-methoxy-1(2H)-naphthalenone (III) was reduced with sodium and alcohol in liquid ammonia [2] at  $-70^\circ$  to 1,2,3,4,5,8-hexahydro-6-methoxy-1-naphthol (VI) in about 80% yield. The use of lithium instead of sodium, in accordance with Wilds and Nelson's modification [3] gave only 24% of the alcohol (VI); The main product was the corresponding pinacol (VII). On hydrolysis of the alcohol (VI) (with simultaneous dehydration) 4,6,7,8-tetrahydro-2(3H)-naphthalenone (VIII) was formed.

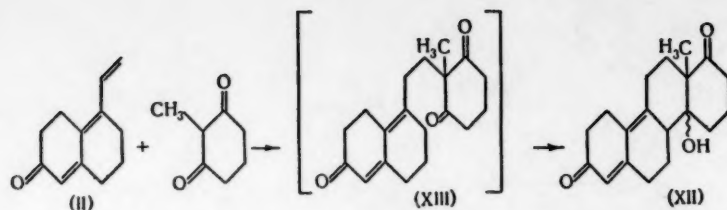
Oppenauer oxidation of the alcohol (VI) gave different results, depending on the reaction conditions. With dry acetone and freshly prepared aluminum isopropoxide there was almost quantitative formation of 3,4,5,8-tetrahydro-6-methoxy-1(2H)-naphthalenone (IX), but the presence of a trace of water in the acetone led to the isomeric 3,4,7,8-tetrahydro-6-methoxy-1(2H)-naphthalenone (IXa) (or a mixture of isomers). It is interesting that oxidation of the alcohol (VI) by Sarett's method [4] is accompanied by dehydrogenation of the ring, and the product is the original 3,4-dihydro-6-methoxy-1(2H)-naphthalenone (III). Analogous cases have been noted in the literature [5,6].

By reaction of the ketone (IX) with vinylmagnesium bromide we obtained 1,2,3,4,5,8-hexahydro-6-methoxy-1-vinyl-1-naphthol (X), and by the hydrolysis of this in an acid medium we obtained the trienone (II). The trienone (II) was found to be a very labile compound which polymerized when kept or heated so that it was impossible to purify it by distillation. Its structure was confirmed by the ultraviolet spectrum: two maxima at 226 and 321  $\text{m}\mu$  ( $\log \epsilon$  4.01; 4.32). The calculated maximum (by Woodward's rule) was 331  $\text{m}\mu$ . For ergosta-4,6,8(14), 22-tetraen-3-one (XI), which is similar in structure, a maximum of 348  $\text{m}\mu$  ( $\log \epsilon$  4.22) is quoted; the value calculated by Woodward's rule is 356  $\text{m}\mu$  [7].



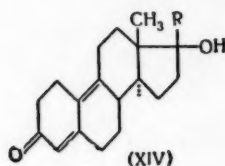
On hydrogenation of the trienone (II) two molecular proportions of hydrogen are absorbed with formation, probably, of the ketone (V). On condensation of the trienone (II) with 2-methyl-1,3-cyclohexanedione in presence of diethylamine the Michael reaction and cyclization occur simultaneously, and 14 $\xi$ -hydroxy-D-homo-19-norandrost-4,9(10)-diene-3,17a-dione (XII) is formed in about 25% yield. We did not succeed in isolating the intermediate triketone (XIII).





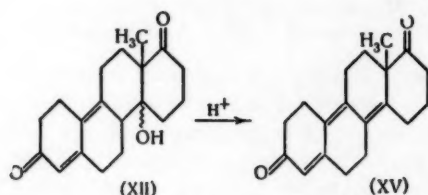
Condensation in presence of benzyltrimethylammonium hydroxide (Triton B) under the conditions described for 2-methyl-3-vinyl-2-cyclohexen-1-one [1] led to complete resinification of the trienone (II).

The structure of the hydroxy diketone (XII) was confirmed by the ultraviolet and infrared spectra. The ultraviolet spectrum had a maximum at 306 m $\mu$  (log  $\epsilon$  4.43) characteristic for cyclic dienones of this type. Thus, for 19-nor- $\Delta^{4,9}$ -3-oxo steroids of the type (XIV) it is stated that [8, 9]  $\lambda_{\text{max}} = 302\text{-}304\text{ m}\mu$  (log  $\epsilon$  4.25-4.32).



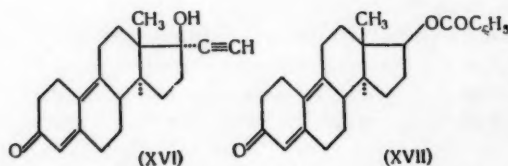
In the infrared spectrum we found the frequencies of an isolated hydroxyl and also of carbonyl groups conjugated with the diene system: 3450, 1703, and 1639  $\text{cm}^{-1}$ , respectively.

The dehydration of the hydroxy diketone (XII) under the action of acids gave D-homo-19-norandrosta-4,8(14), 9(10)-triene-3,17a-dione (XV), which was prepared recently by Zav'yalov and co-workers [10].

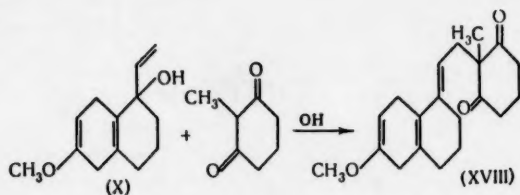


The configurations at the asymmetric centers C-(8), C-(14), and C-(13) in the diketone (XII) have not been established and will be the subject of further investigations.

Thus, starting with the accessible 3,4-dihydro-6-methoxy-1(2H)-naphthalenone, we effected the synthesis of the  $\Delta^{4,9}$ -3-oxo steroid. Judging from recent literature, steroids of this type are of interest as physiologically active substances; for example 17-ethynyl-17 $\beta$ -hydroxy-19-norandrosta-4,9(10)-dien-3-one (XVI) was found to be considerably more active than the well known gestagenic hormone norlutin [8]. The benzoic ester of 17 $\beta$ -hydroxy-19-norandrosta-4,9(10)-dien-3-one (XVII) was recently prepared by total synthesis from 3,4-dihydro-6-methoxy-1(2H)-naphthalenone [11].



We carried out also the condensation of the ethylenic alcohol (X) with 2-methyl-1,3-cyclohexanedione under the conditions described earlier [12] for 1,2,3,4-tetrahydro-6-methoxy-1-vinyl-1-naphthol; we then obtained a low yield (10%) of the expected reaction product, 3-methoxy-8,14-seco-D-homoestra-2,5(10), 9(11)-triene-14,17a-dione (XVIII).



The infrared spectrum of the methoxy diketone (XVIII) contains bands at 1721 and 1698  $\text{cm}^{-1}$ , characteristic for disubstituted 1,3-cyclohexane-diones [13].

## EXPERIMENTAL

**Reduction of 1,2,3,4-Tetrahydro-6-methoxy-1-vinyl-1-naphthol (IV) by Birch's Method.** Sodium (15 g) was added in small portions at from  $-60^{\circ}$  to  $-70^{\circ}$  over a period of two hours to a mixture of 160 ml of liquid ammonia, 100 ml of absolute methanol, and 6.2 g of the ethylenic alcohol (IV); a further 50 ml of absolute methanol was added, the cooling bath was removed, the ammonia was allowed to evaporate, 600 ml of water was added, and the reaction mixture was extracted three times with ether. Ether was distilled off, and the residue was mixed with 50 ml of 10% sulfuric acid and refluxed with stirring for four hours. The mixture was cooled and extracted with ether; the extract was dried with sodium sulfate, ether was distilled off, and the residue was twice vacuum-distilled. We obtained 2.5 g (39%) of 1-ethyl-4,4a,5,6,7,8-hexahydro-2(3H)-naphthalenone (V); b.p.  $80-83^{\circ}$  (0.5 mm);  $n_D^{20}$  1.5123. Found: C 80.74; 80.93; H 10.20; 10.22%.  $\text{C}_{12}\text{H}_{18}\text{O}$ . Calculated: C 80.85; H 10.18%.

**Reduction of 3,4-Dihydro-6-methoxy-1(2H)-naphthalenone.** By Birch's Method [2]. Sodium (34.5 g) was added over a period of one hour at from  $-73^{\circ}$  to  $-74^{\circ}$  to a solution of 30 g of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone in 1 liter of liquid ammonia and 360 ml of absolute alcohol. After the discolorization of the dark-blue mixture (10-15 minutes), the temperature was gradually raised to  $-20^{\circ}$ ; the cooling bath was removed, and ammonia was evaporated in a feeble current of nitrogen. Ether (150 ml) was added to the residue, and at  $-10^{\circ}$  water (780 ml) was added with stirring. After ten minutes the ether layer was separated, and the aqueous layer was extracted eight times with ether. The combined ether layers were washed twice with saturated brine and once with water; they were dried with anhydrous potassium carbonate. After removal of solvent and addition of petroleum ether, the residue crystallized out. We obtained 23.3 g (77%) of 1,2,3,4,5,8-hexahydro-6-methoxy-1-naphthol (VI), m.p.  $71-73^{\circ}$ . After two crystallizations from petroleum ether the product had: m.p.  $73-74^{\circ}$ ;  $\lambda_{\text{max}}$  (in alcohol)  $m\mu$  (log  $\epsilon$  2.23). The literature [2] gives m.p.  $73-74^{\circ}$ . Judging from the ultraviolet spectrum this alcohol contained a little of its isomer with a conjugated diene system.

**By Wilds and Nelson's Method [3].** Lithium (6.9 g) was added in small pieces over a period of 20 minutes at  $-67^{\circ}$  to  $-68^{\circ}$  to a solution of 13 g of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone in 225 ml of dry ether and 500 ml of liquid ammonia. After 15 minutes, 118 ml of absolute alcohol was added over a period of 30 minutes (when the reaction mixture, which had a dark-blue color with a bronze reflex, was decolorized). After a further period of 10-15 minutes the bath temperature was gradually raised to  $-20^{\circ}$ ; the cooling bath was removed, and ammonia was evaporated in a feeble current of nitrogen. Ether (50 ml) and water (400 ml) were added to the residue at  $-5^{\circ}$ . The ether layer was separated, and the aqueous layer was repeatedly extracted with ether. The combined extracts were washed twice with saturated brine and dried with anhydrous potassium carbonate. Solvents were distilled off, and to the residue we added 20 ml of petroleum ether (b.p.  $45-65^{\circ}$ ) and 5 ml of a mixture of ether and methanol. The precipitate formed was washed with ether, and we obtained 4.85 g (37%) of 1,1',2,2',3,3',4,4',5,5',8,8'-dodecahydro-6,6'-dimethoxy-1,1'-bi-1-naphthol (VII), m.p.  $181-183^{\circ}$ . An analytical preparation had m.p.  $187-189^{\circ}$  (from alcohol). Found: C 73.52; 73.44; H 7.75; 7.60%; mol. wt. (Rast) 334.  $\text{C}_{22}\text{H}_{30}\text{O}_4$ . Calculated: C 73.70; H 8.31%; mol. wt. 359. By evaporation of the mother solutions and vacuum distillation we isolated 3.1 g (24%) of the alcohol (VI); b.p.  $115-125^{\circ}$  (0.7 mm)  $72-74^{\circ}$ .

Hydrolysis of the Alcohol (VI). A solution of 2 g of the alcohol (VI) in 40 ml of ether was stirred with 13 ml of 10% hydrochloric acid for two hours. The ether layer was separated, and the aqueous layer was extracted twice with ether. Fractionation gave 1.25 g (81%) of 4,6,7,8-tetrahydro-2(3H)-naphthalenone (VIII); m.p. 74-75° (1.2 mm);  $n_D^{20}$  1.5792;  $\lambda_{\max}$  (in alcohol) 287 m $\mu$  (log  $\epsilon$  3.99). An analytical sample had  $n_D^{20}$  1.5800. Found: C 80.72; 80.92; H 8.11; 8.01%  $C_{16}H_{12}O$ . Calculated: C 81.04; H 8.16%. The 2,4-dinitrophenylhydrazone had m.p. 204-206°;  $\lambda_{\max}$  (in alcohol) 395 m $\mu$  (log  $\epsilon$  4.46). Found: N 16.98; 16.88%  $C_{16}H_{10}O_4N_4$ . Calculated N 17.05%.

Oxidation of the Alcohol (VI). By the Oppenauer Method. A mixture of 14.1 g of the alcohol (VI) and 3.1 g of aluminum isopropoxide in 42 ml of dry acetone and 48 ml of dry toluene was boiled in a current of nitrogen for six hours. Ether (20 ml) and water (30 ml) were added to the cooled solution, the organic layer was separated, and the aqueous layer was extracted three times with ether. The extract was dried with magnesium sulfate, solvents were distilled off, and the residue was caused to crystallize by rubbing it out with petroleum ether. We obtained 13.3 g (94%) of the ketone (IX), m.p. 45-47°;  $\lambda_{\max}$  (in alcohol) 239 m $\mu$  (log  $\epsilon$  3.98). The literature [7] gives m.p. 46-48°. When acetone containing 0.1% of water was used, a 72% yield was obtained of the isomer (IXa); b.p. 115-117° (0.5 mm)  $n_D^{21}$  1.5743;  $\lambda_{\max}$  (in alcohol) 276 m $\mu$  (log  $\epsilon$  4.02).

Both of the ketones (IX) and (IXa) gave the same dioxime, m.p. 181-182° (from alcohol). For the melting point of the dioxime the literature [2] gives 181-183°.

By Sarett's Method. A solution of 0.7 g of the alcohol (VI) in 8 ml of dry pyridine was added with shaking over a period of five minutes to the complex prepared from 1.19 g of chromium trioxide and 5 ml of dry pyridine. After one day the mixture was poured into 150 ml of water and carefully extracted with ether and benzene. Solvents were distilled off from the dried (magnesium sulfate) extract, and the extract crystallized out when rubbed out with petroleum ether; it was filtered off and washed with hexane. We obtained 0.61 g (87%) of 3,4-dihydro-6-methoxy-1(2H)-naphthalenone(III); m.p. 76-77° (from methanol;  $\lambda_{\max}$  (in alcohol) 275.5 m $\mu$  (log  $\epsilon$  4.20). A mixture test with a known sample showed no depression of melting point.

Preparation of 1,2,3,4,5,8-Hexahydro-6-methoxy-1-vinyl-1-naphthol (X). With stirring and passage of nitrogen, 15.9 g of the ketone (IX) in 70 ml of ether and 20 ml of tetrahydrofuran was added at -20° to a solution of vinylmagnesium bromide (prepared from 8 g of magnesium, 50 g of vinyl bromide, and 105 ml of dry tetrahydrofuran). After one day the mixture was boiled for 90 minutes, cooled, and poured on a mixture of 42 g of ammonium chloride and 220 g of ice (temperature about -5°). The organic layer was separated, the aqueous layer was extracted with ether, and the extract was dried with magnesium sulfate. After removal of solvents we obtained 17.4 g of the ethylenic alcohol (X) as a yellow oil,  $n_D^{23}$  1.5426.

Analogously, from the ketone (IXa) we obtained the isomer of this ethylenic alcohol;  $n_D^{28}$  1.5608.

Preparation of the Trienone (II). To a solution of 14.1 g of the ethylenic alcohol (IX) in 100 ml of ether we added 25 ml of 10% hydrochloric acid and 0.05 g of pyrogallol. The mixture was stirred in a stream of nitrogen for 2.5 hours, the ether layer was separated, and the aqueous layer was extracted twice with ether. The combined ether extracts were washed four times with saturated sodium bicarbonate solution and once with water, and they were dried with magnesium sulfate at 0°. After removal of solvent (bath temperature not above 40°) we obtained 10.8 g (90%) of the trienone (II) as a fairly mobile yellow oil. The ketone(II) polymerizes at ordinary temperatures and still more rapidly when heated; it must be used in syntheses without delay;  $n_D^{21}$  1.6304;  $\lambda_{\max}$  (in alcohol) 226 and 321 m $\mu$  (log  $\epsilon$  4.01 and 4.23).

Hydrogenation of the Trienone (II). The trienone (II) (1.07 g) was hydrogenated in isopropyl alcohol (50 ml) over previously reduced 10% palladium on strontium carbonate (0.15 g) until two molecular proportions of hydrogen had been absorbed. Solvent was distilled off, and vacuum distillation of the residue gave 0.75 g (70%) of the ketone (V); b.p. 107-110° (1 mm)  $n_D^{21}$  1.5081;  $\lambda_{\max}$  (in alcohol) 240 m $\mu$  (log  $\epsilon$  3.68). Found: C 80.67; 80.59; H 10.29; 10.47%.  $C_{12}H_{18}O$ . Calculated: C 80.85; H 10.18%.

Condensation of the Trienone (II) with 2-Methyl-1,3-cyclohexanedione in Presence of Diethylamine. A mixture of 5 g of the trienone ( $n_D^{21}$  1.6302), 3.56 g of 2-methyl-1,3-cyclohexanedione, 2.6 g of diethylamine, 8 ml of dry benzene, 6.5 ml of dry t-butyl alcohol, and 50 mg of pyrogallol was heated with stirring at 50° in a current of nitrogen until the methylcyclohexanedione dissolved completely (38 hours). Ether (70 ml) and methylene chloride (150 ml) were added to the cooled dark-brown mass; the resulting solution was washed four times with saturated sodium bicarbonate solution, three times with 10% hydrochloric acid, and once with water; it was dried with magnesium sulfate. Solvents were distilled off, and the residual dark-brown oil (6.01 g) was dissolved in a 1:1 mixture of

benzene and methylene chloride and adsorbed in a column containing 190 g of alumina (activity II). Elution with benzene gave 1.7 g of a dark-brown oil, which did not crystallize out and did not distill without decomposition. From the fractions eluted with a 1:1 mixture of benzene and chloroform and with pure chloroform we obtained 1.98 g (24%) of the hydroxy diketone (XII) in the form of light-yellow crystals, m.p. 201-205°. An analytical preparation had: m.p. 207-209° (from alcohol);  $\lambda_{\max}$  (in alcohol) 306 m $\mu$  ( $\log \epsilon$  4.43); infrared spectrum 1703, 1639, 1613, 1580, 3450  $\text{cm}^{-1}$ . Found: C 75.86, 75.66; H 8.17; 8.13%  $\text{C}_{19}\text{H}_{24}\text{O}_3$ . Calculated: C 75.97; H 8.05%.

Dehydration of the Hydroxy Diketone (XII) to Give the Trienedione (XV). A mixture of 0.28 g of the hydroxy diketone (XII), 50 mg of p-toluenesulfonic acid, and 6.5 g of glacial acetic acid was boiled for two hours. When the mixture was cool, acetic acid was vacuum-distilled off, the residue was diluted with 40 ml of benzene, and the resulting liquid was washed with sodium bicarbonate solution and dried with magnesium sulfate. The oil (0.19 g) remaining after the removal of benzene was dissolved in 25 ml of a 1:1 mixture of benzene and chloroform and adsorbed on a column containing 5 g of alumina (activity II). Elution with a 1:1 mixture of benzene and ether gave 41 mg of a yellow oil, from which, by rubbing it out with petroleum ether and alcohol, we obtained 28 mg (11%) of the dione (XV), m.p. 99-100°.

A mixture test with a known sample showed no depression of melting point. The literature [10] gives m.p. 100-102°. On chromatography on plates (alumina of activity V, thickness 1-1.5 mm, 1:1 benzene-ether, development with  $\text{H}_2\text{SO}_4$ ) the two samples gave spots of identical  $R_f$ . From the 1:1 benzene-chloroform fraction we obtained 38 mg of the original hydroxy diketone (XII), m.p. 200-202°.

Condensation of 1,2,3,4,5,8-Hexahydro-6-methoxy-1-vinyl-1-naphthol (X) with 2-Methyl-1,3-cyclohexanedione. In a stream of nitrogen 4.12 g of the ethylenic alcohol (X) in 5 ml of p-xylene was added with stirring to a mixture of 2.52 g of 2-methyl-1,3-cyclohexanedione, Triton B (prepared from 0.54 g of benzyltrimethylammonium chloride and 0.16 g of potassium hydroxide in 5 ml of alcohol), 8 ml of toluene, and 5 ml of p-xylene at 130-135°; heating was continued at this temperature for 90 minutes, and then at 143-146° for one hour. A mixture of toluene, xylene, and water was then distilled off. When water ceased to separate, 50 ml of ether was added to the cooled mixture, and unchanged methylcyclohexanedione (1.25 g) was filtered off. The filtrate was washed three times with 5% sodium hydroxide solution and twice with water; it was dried with magnesium sulfate. Solvents were distilled off, and we then obtained 3.12 g of yellow oil, from which, after rubbing out with ether and cooling with solid carbon dioxide, we succeeded in isolating 0.28 g of the diketone (XVIII) in the form of crystals of m.p. 120-129°. An analytical sample had m.p. 124-126° (from alcohol);  $\gamma_{\max}$  (in alcohol) 243 m $\mu$  ( $\log \epsilon$  4.17); infrared spectrum: 1721, 1698, 1598, 1563  $\text{cm}^{-1}$ . Found: C 76.68; 76.77; H 8.26; 8.28%  $\text{C}_{20}\text{H}_{26}\text{O}_3$ . Calculated: C 76.49; H 8.31%. From the mother liquor we isolated a further 0.31 g of the product, m.p. 121-125°. The total yield of the diketone (XVIII) was 10%.

#### SUMMARY

1. 4,6,7,8-Tetrahydro-5-vinyl-2(3H)-naphthalenone (II), an intermediate for the synthesis of 19-nor- $\Delta^{4,9}$ -3-oxo steroids, was prepared in four stages from 3,4-dihydro-6-methoxy-1(2H)-naphthalenone (III).

2. In the condensation of the trienone (II) with 2-methyl-1,3-cyclohexanedione, 14 $\xi$ -hydroxy-D-homo-19-norandrost-4,9(10)-diene-3,17a-dione (XII) is formed, and the dehydration of this in an acid medium gives D-homo-19-norandrost-4,8(14),9(10)-triene-3,17a-dione (XV).

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# HETEROGENEITY OF NITROLIGNIN

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We have previously studied the nitration of isolated lignins [1] and lignin models: derivatives of 2-methoxy-4-propylphenol and 1,2-dimethoxy-4-propylbenzene [2], and also 1-(3,4-dimethoxyphenyl)-2-o-methoxyphenoxy-1,3-propanediol [3]. With the object of obtaining a more profound understanding of the process of the nitration of lignin, work has been continued with lignin that has not been isolated from the wood. Many investigations on the nitration of nonisolated lignins are associated with the delignification of vegetable material [4], and the nitration has been carried out with dilute nitric acid at 80-100°. It is known that the treatment of lignin with dilute nitric acid at a high temperature leads not only to the nitration of the lignin, but also to its oxidative degradation.

Of these methods, that proposed by Kürschner and Hoffer [5] for the nitration of lignin is noteworthy. In this method wood flour is nitrated with an alcoholic solution of nitric acid (1 vol. of HNO<sub>3</sub>, sp. gr. 1.4, and 4 vol. of ethanol). Nitration in alcoholic solution reduces the degradative effect of nitric acid on lignin, and it is possible that such nitrolignin preparations contain a relatively smaller amount of degradation products, which must facilitate its investigation.

We prepared preparations of nitrolignin by three treatments of fir wood with a mixture of nitric acid, sp. gr. 1.4, and ethanol under the conditions of Kürschner's method. The resulting nitrolignin was separated into three fractions in accordance with the alcohol-solubility: insoluble in ethanol (13-15%); soluble only in hot ethanol (11-14%); soluble in cold ethanol (70-75%). For purification the last was dissolved in cold ethanol and passed through a column of MgO adsorbent. As a result we obtained a chromatogram with three adsorption zones and unadsorbed nitrolignin. The first zone (from the top downward) was brown; the second zone was light yellow, and the third was light brown.

The solubility of MgO in dilute mineral acids, and the stability and low solubility of nitrolignin in dilute nitric acid made it possible to isolate nitrolignins from the adsorbent with losses of not more than 23%. The results are given in Table 1.

TABLE 1.

Amt. of nitrolignin taken for chromatography (g)	Amt. of nitrolignin isolated (g)			Amt. of unadsorbed nitrolignin (g)
	from first zone	from second zone	from third zone	
4.9195	2.5634	1.208	0.2	0.025
1.990	0.7370	0.4677	0.101	0.24
0.3001	0.1515	0.071	0.01	

The C, H, and N contents of all nitrolignin preparations were determined.

The nitrolignins (crude, reprecipitated, insoluble in ethanol, and products isolated from the first and second adsorption zones) were analyzed for OCH<sub>3</sub>, COOH, CHO, and OH contents. Methoxyl content was determined by Bühn's method, carboxyl by Purves's method [6], and carbonyl by Lindberg's method [7], by reduction with sodium borohydride; hydroxy groups were determined by Verley's acylation method. The results are given in Table 2.

The experiments showed that the nitrolignin preparations were heterogeneous. Their main components were the products isolated from the first and second adsorption zones. As will be seen from Table 2, the



TABLE 2.

Nitrolignin	C, %	H, %	N, %	OCH <sub>3</sub> , %	COOH, %	CO(H), %	OH, %	Mol. wt. by cryoscopic method
Nitrolignin (crude product)	51.19	5.29	4.44	11.61	4.28	6.60	7.57	
Nitrolignin [5] re-precipitated from ethanol	52.14	5.36	3.63	10.12	4.89	4.04	8.3	
Nitrolignin insoluble in ethanol	51.97	5.14	3.47	10.61	3.52	3.13		
Nitrolignin isolated from the first adsorption zone	52.17	4.99	4.17	13.73	6.03	3.2	9.07	634 (in dioxane)
Nitrolignin isolated from the second adsorption zone	52.76	5.42	4.10	14.76	5.01	4.5	6.6	2000 (in dioxane)
Nitrolignin isolated from the third adsorption zone	56.36	6.00	4.26					
Nitrolignin not adsorbed by MgO	62.13	7.73	2.79					
Nitrolignin soluble only in hot ethanol	51.25	5.08	3.91					

nitrolignins differ in their carbonyl and hydroxyl contents and in molecular weight. The molecular weight of the nitrolignin isolated from the first adsorption zone was 634 (determined cryoscopically in dioxane). The molecular weight of the nitrolignin isolated from the second adsorption zone was 2000 (determined cryoscopically in dioxane). It may be supposed that the nitrolignins are fractionated in accordance with their molecular sizes.

#### EXPERIMENTAL

Nitrolignin was prepared by the treatment of fir chippings (20 g; age of fir 16 years), previously extracted with ethanol and dichloroethane, with a mixture (250 ml) of ethanol (4 volumes) and nitric acid of sp. gr. 1.4 (1 volume). The nitration was carried out in a flask fitted with reflux condenser with heating in a water bath (temperature 72°) for two hours with slow stirring. The chippings were filtered off and treated twice further with the mixture of ethanol and nitric acid. Nitrolignins were isolated by the addition of water to the three filtrates. The nitrolignins were filtered off and washed with distilled water until the acid reaction disappeared. The sample were dried to constant weight in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>. The nitrolignin preparations had a light-yellow color. The total yield of nitrolignin was about 15% (on the weight of chippings taken).

Ethanol (100 ml) was added to the nitrolignin obtained (7 g); most of the nitrolignin then went into solution. The insoluble part of the nitrolignin was filtered off. The weight of the nitrolignin that did not dissolve in cold ethanol was about 2 g. The filtrate was passed through an MgO column. We obtained a chromatogram with three adsorption zones and a small amount of unadsorbed nitrolignin. The adsorbent was dried out, and the column was discharged. The separate zones of the adsorbent were mixed with 100-150 ml of ethanol, and the mixture was slowly added to excess of dilute nitric acid. The MgO was dissolved, and the nitrolignins were precipitated; they were filtered off, washed with water, and dried. For purification, the nitrolignins were again dissolved in ethanol and separated by addition of dilute nitric acid. The results of the experiments are given in Table 1.

## SUMMARY

1. A chromatographic investigation was carried out on nitrolignin preparations obtained by the treatment of nonisolated lignin (fir wood chippings) with a mixture of ethanol and nitric acid, sp. gr. 1.4, under the conditions of Kürschner's method.

2. Chromatograms were obtained with three adsorption zones, which indicates the heterogeneity of the original nitrolignin. The nitrolignin of lower molecular weight was adsorbed in the upper layers of the column, and the nitrolignin of higher molecular weight was adsorbed lower down.

3. The work carried out enables us to pose the question of whether natural lignin is homogeneous so that the two main components obtained are formed only as a result of degradation occurring during nitration, or whether they are the nitration products of a mixture of natural lignins.

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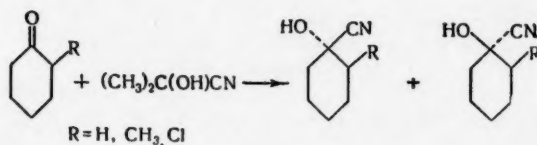
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# RAMAN-SPECTRUM INVESTIGATION OF THE CONFORMATIONS OF THE CYANOHYDRINS OF SOME CYCLOHEXANONE DERIVATIVES

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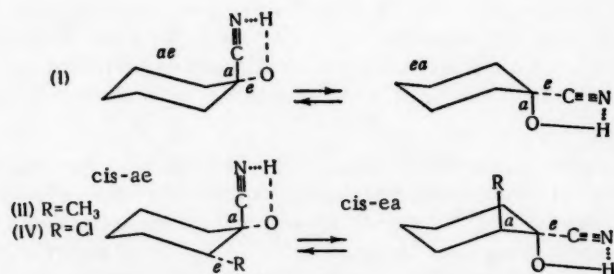
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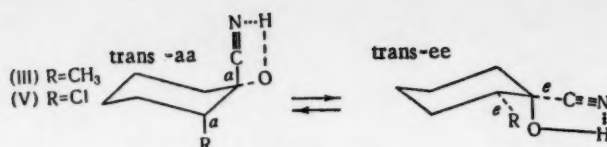
The compounds investigated were prepared by two of us [1] in accordance with the scheme:



When  $R = CH_3$  or  $Cl$  cis-trans isomerism is possible on account of the different mutual positions of the largest substituents  $CN$  and  $R$ . In the case of 2-chloro-1-hydroxycyclohexanecarbonitrile two isomers could not be isolated; the product had m.p. 29-31°; its configuration was not determined. 1-Hydroxy-2-methylcyclohexanecarbonitrile was obtained as a mixture of two isomers which differed sharply in melting point: one was a liquid, and the other was a crystalline solid, m.p. 53-54°. The latter was isolated in an almost pure state by crystallization, but the liquid isomer could not be separated from dissolved crystalline isomer. In the present work we attempted to determine the configurations and conformations of the four substances obtained by examination of the Raman spectra and by considerations based on our previous investigations (see references 1 and 8 in [2]). The Raman spectrum of a mixture of cis- and trans-1-hydroxy-2-methylcyclohexanecarbonitriles was determined in the liquid state at about 25°; those of the other three substances were determined in the supercooled molten state at about 25°.

In the spectrum of 1-hydroxycyclohexanecarbonitrile (the cyanohydrin of cyclohexanone) (I) the hydroxyl frequencies form a narrow band at about 3400-3475  $cm^{-1}$ , which is characteristic for a hydroxyl taking part in an intramolecular hydrogen bond [3]. The doublet character of the frequency of the pulsating frequency of the cyclohexane ring (656, 674  $cm^{-1}$ ) and also of the vibration frequency of the cyano group (2226, 2239  $cm^{-1}$ ) indicates the existence of (I) in two conformations *ae* and *ea*. Under the experimental conditions (supercooled fused state) neither conformation is substantially predominant, as may be judged from the intensities of the frequencies of the doublets (see table).





Vibration Frequencies of OH, CN, CCl, and the Cyclohexane Ring

Group	(I)	(II)	Mixtures of (II) and (III)	(IV) with admixed (V)
OH	~3400—3475 band	~3400—3480 band	~3400—3480 band	~3340—3530 band
C≡N	2226(9*) 2239(9*)	2224(4*) 2233(7*)	{ 2219(3*) 2226(8*) 2234(6*)	{ 2222(2*) 2229(8*) 2237(6*)
C—Cl				752(5*) } 794(1**) 761(3*) } 812(1**)
	656(7sh*) 674(7sh*)	644(7sh*) 652(9sh*) 695(0**) 701(0**)	645(5*) 650(7*) 694(5**) 701(6**)	666(5*) 676(7*) 702(2**) 720(2**)

\*Slightly blurred at the lower-frequency side.

In the spectrum of the crystalline 1-hydroxy-2-methylcyclohexanecarbonitrile, determined in the supercooled fused state, there is an intense doublet associated with the pulsating vibration of the cyclohexane ring (644, 652 cm<sup>-1</sup>) and a doublet at a higher frequency (695, 701 cm<sup>-1</sup>) corresponding to a substance present in small amount. The intensity of the latter doublet is much greater (see table) in the spectrum of the liquid mixture of isomers [sample of b.p. 96-97° (5mm)]. According to our previous investigations (see references 1 and 8 in [2]), the doublet of the lower frequency is to be attributed to the cis-configuration (II), and that of the higher frequency to the trans-configuration (III). Hence, the crystalline product of m.p. 53-54° is almost pure cis-1-hydroxy-2-methylcyclohexanecarbonitrile (II), and the liquid product of b.p. 96-97° (5 mm) is a mixture of cis- and trans-1-hydroxy-2-methylcyclohexanecarbonitriles [(II) + (III)] with some predominance of the cis-form (II). The doublet character of the vibration frequencies of the ring is probably due to the presence of two conformations, both in (II) and in (III). This view is confirmed by the doublet character (224, 2233 cm<sup>-1</sup>) of the vibration frequencies of the cyano group in (II) and the superposition of doublets (2219, 2226, 2226, 2234 cm<sup>-1</sup>) in the mixture of (II) = (III); the intensity of the middle line (2226 cm<sup>-1</sup>) is raised because of the superposition of the extreme lines of the doublets (see table). If we consider, in accordance with Barton and Hassel's rule (see references 1 and 8 in [2]), that the largest substituent (cyano group) tends to occupy the equatorial position, then, judging from the intensities, the equatorial cyano group in (II) has a higher frequency (2233 cm<sup>-1</sup>) than the axial group (2224 cm<sup>-1</sup>), and in (II) the conformation cis-ee is somewhat predominant. The vibration frequencies in (III) are lower (2219, 2226 cm<sup>-1</sup>); in this configuration the conformation trans-ee is more predominant, and this has the more intense frequency 2226 cm<sup>-1</sup>, the above-noted superposition of the extreme frequencies of two doublets being taken into account. The intense narrow band of the hydroxyl frequency in (II) and in the mixture of (II) and (III) indicates the participation of the hydroxyl in an intramolecular hydrogen bond in these substances. The slight blurring of the band on the lower-frequency side indicates the perturbing effect of oxygen and nitrogen atoms of neighboring molecules on the hydroxyl; but only in an extremely small number of molecules can this action result in the formation of an intermolecular hydrogen bond with cleavage of the intramolecular bond.

In the spectrum of 2-chloro-1-hydroxycyclohexanecarbonitrile there are two doublets associated with the pulsating vibration of the cyclohexane ring: a lower frequency doublet of higher intensity (666, 676 cm<sup>-1</sup>) and a high-frequency one of low intensity (702, 720 cm<sup>-1</sup>); the first belongs (see references 1 and 8 in [2]) to the cis-configuration (IV) and the second to the trans-configuration (V). In the mixture the cis-configuration is predominant (80% or more); this is indicated also by the vibration frequencies of the C-Cl bond (see table). The doublet



characters of the frequencies of the ring, the C-Cl bond, and the cyano group indicate that each of the configurations exist in two conformations. The more intense high frequency of the high-frequency doublet of the cyano group (equatorial) and the more intense low frequency in the low-frequency doublet of the vibration frequencies of the C-Cl bond (axial) indicate a predominance of the conformation *cis-ea*. The band of the hydroxyl included in the intramolecular hydrogen bond  $-C \equiv N \dots H-O-$  is broadened (about 3340-3530  $\text{cm}^{-1}$ ) because of the perturbing intramolecular effect of the chlorine atom, which endeavors to form the intramolecular hydrogen bond  $-Cl \dots H-O-$ , which is characterized by a higher-frequency hydroxyl band [3], and also because of the perturbing intermolecular effect of the nitrogen, oxygen, and chlorine atoms of other molecules, which cause the hydroxyl band to be blurred on the low-frequency side. However, it appears that in this case also there are only a few molecules for which an intramolecular hydrogen bond or the above-indicated intermolecular hydrogen bonds are formed.

#### EXPERIMENTAL

Below we give the physical constants of the compounds investigated.

	M.p. ( $^{\circ}\text{C}$ )	B.p. in $^{\circ}\text{C}$ (p in mm)	$n_D^{20}$
(I)	34-36	104(5)	1.4653
(II)	53-54	96-97(5)	
(II) + (III), mixture	-	96-97(5)	1.4670
(IV) with admixed (V)	29-31	113.5-114(5)	1.4820

The Raman spectra were determined in the liquid phase with a Soviet ISP-51 spectrograph with a central camera and with a Hilger E6-12 spectrograph; the exciting radiation was the blue line at 4358 Å from the mercury lamp (for the abbreviations with the intensities see [2]):

1-Hydroxycyclohexanecarbonitrile ( $\Delta\nu$ ,  $\text{cm}^{-1}$ ): 123 (3\*), 134 (3\*), 158 (4\*\*), 171 (2\*\*), 208 (3\*), 218 (3\*), 261 (0), 388 (3), 419 (3\*), 433 (3\*), 453 (3\*), 479 (0), 505 (0), 532 (0), 623 (2db), 656 (7\*sh), 674 (7\*sh), 746 (3db), 815 (5), 836 (2), 857 (2), 901 (1), 991 (0), 1031 (7), 1066 (6), 1076 (0\*), 1090 (0\*), 1103 (0\*), 1130 (1), 1161 (2), 1181 (1), 1199 (0), 1262 (7\*), 1277 (5\*), 1333 (0\*\*), 1350 (2\*\*), 1441 (10\*db), 1462 (2\*), 2226 (9\*\*), 2239 (9\*\*), 2853 (9\*), 2866 (9\*), 2920 (2\*\*), 2931 (10\*\*), 2946 (10\*\*), 2964 (3\*\*), ~3400-3475 (3 band).

*cis*-1-Hydroxy-2-methylcyclohexanecarbonitrile ( $\Delta\nu$ ,  $\text{cm}^{-1}$ ): 115 (3\*), 126 (3\*), 152 (8sh\*\*), 159 (4\*\*), 170 (4\*\*), 225 (3b db), 288 (2db), 335 (2 db), 360 (1), 413 (3 db), 451 (4db), 470 (4db), 613 (3), 644 (7\*sh), 652 (9sh\*), 695 (0\*\*), 701 (0\*\*), 799 (2db), 839 (4), 862 (3), 986 (6\*), 999 (6\*), 1047 (1sh\*\*), 1059 (1sh\*\*), 1070 (3\*), 1080 (3\*\*), 1124 (6db), 1166 (7db), 1186 (0), 1224 (4b, db), 1262 (8db) 1329 (3\*), 1345 (3\*), 1356 (3\*), 1441 (6\*\*), 1450 (10\*\*), 1462 (2\*\*), 1476 (0\*\*), 2224 (4\*), 2233 (7\*), 2857 (7\*\*), 2868 (7\*\*), 2921 (3\*\*), 2931 (10\*\*), 2942 (8\*\*), 2953 (3\*\*), 2971 (1\*\*), 2988 (1\*\*), ~3400-3480 (4, band with slight blurring on low-frequency side).

Mixture of *cis*- and *trans*-1-hydroxy-2-methylcyclohexanecarbonitrile ( $\Delta\nu$ ,  $\text{cm}^{-1}$ ): 116 (3\*), 125 (3\*), 150 (6\*\*), 153 (3\*\*), 159 (5\*\*), 169 (4\*\*), 177 (1\*\*), 187 (1\*\*), 223 (3b, db), 288 (2 db), 301 (0), 336 (2db), 360 (1), 388 (0), 400 (3\*), 414 (3\*db), 451 (3db), 460 (4\*db), 470 (4\*db), 485 (0), 496 (1), 510 (0), 538 (1), 548 (1), 569 (0), 579 (0), 589 (1\*), 596 (1\*), 613 (2\*\*db), 622 (1\*\*), 645 (5\*), 650 (7\*), 573 (1sh\*\*), 679 (1sh\*\*), 694 (5\*), 701 (6\*), 758 (0), 798 (2db), 828 (4\*), 839 (4\*), 850 (0), 862 (3), 882 (0\*), 892 (0\*), 904 (1\*\*), 913 (1\*\*), 973 (3\*), 987 (5\*), 996 (6\*), 1048 (1\*\*), 1058 (3\*\*), 1065 (3\*\*), 1071 (1\*\*), 1080 (1\*\*), 1125 (6db), 1158 (6\*), 1167 (7\*), 1187 (0), 1224 (4b db), 1263 (8db), 1308 (1), 1329 (2\*), 1339 (2\*), 1346 (4\*), 1357 (3\*), 1441 (5\*\*), 1450 (10\*\*) 1463 (5\*\*), 1475 (1\*\*), 2219 (3\*), 2226 (8\*), 2234 (6\*), 2857 (7\*\*), 2869 (7\*\*), 2905 (1\*\*), 2920 (3\*\*), 2932 (10\*\*), 2943 (10\*\*), 2954 (7\*\*), 2972 (3\*\*), 2990 (3\*\*), ~3400-3480 (4, band with slight blurring on low-frequency side).

*cis*-(and admixed *trans*)-2-chloro-1-hydroxycyclohexanecarbonitrile ( $\Delta\nu$ ,  $\text{cm}^{-1}$ ): 107 (4\*), 120 (4\*), 139 (8sh\*\*), 165 (4\*\*), 172 (4\*\*), 181 (1\*\*), 229 (4b, db, band), 314 (6), 342 (3db), 395 (3 db), 428 (7), 445 (0), 458 (2db), 493 (1db), 526 (1), 559 (1\*), 573 (1\*) 599 (6), 666 (5\*), 676 (7\*), 702 (2\*\*), 720 (2\*\*), 752 (5\*), 761 (3\*), 794 (1\*\*), 812 (1\*\*), 855 (6 db), 896 (4), 927 (0\*), 941 (0\*), 965 (5\*), 999 (0,sh), 1032 (2\*), 1044 (6\*), 1071 (6), 1087 (0), 1104 (3), 1137 (4\*), 1151 (4\*), 1213 (4), 1236 (4), 1261 (5), 1278 (0,db), 1302 (0, db), 1338 (6), 1355 (0), 1448 (8\* b, db), 1461 (0\*), 2222 (2\*\*), 2229 (8\*\*), 2237 (6\*\*) 2861 (7\*), 2872 (7\*), 2898 (2\*), 2914 (3\*), 2929 (3\*), 2936 (8sh\*), 2947 (10sh\*), 2963 (5sh\*), 2976 (2sh\*), ~3340-3530 (4, band).



## SUMMARY

1. Cyclohexanone cyanohydrin (1-hydroxycyclohexanecarbonitrile) (I) exists in two conformation ae and ea, neither of which predominates appreciably over the other.

2. The crystalline 1-hydroxy-2-methylcyclohexanecarbonitrile investigated was found to be almost pure cis-isomer (II), whereas the liquid form was a mixture of the cis- and trans-isomers (II) + (III); in the cis-configuration the conformation cis-ea is somewhat predominant, while in the trans-configuration the conformation trans-ee predominates.

3. The 2-chloro-1-hydroxycyclohexanecarbonitrile investigated is a mixture of cis- and trans-configurations (IV), in which the cis-configuration predominates substantially (about 80%); the predominant conformation is cis-ea.

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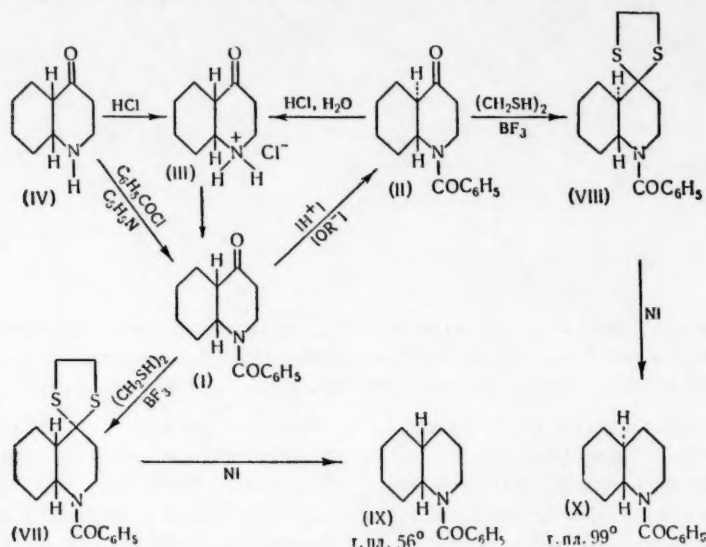
## STEREOCHEMISTRY OF HETEROCYCLIC COMPOUNDS

COMMUNICATION 7. STERIC STRUCTURES OF OCTAHYDRO-4(1H)-QUINOLONE  
DERIVATIVES AND THE CONFIGURATIONS OF DECAHYDROQUINOLINES

É. A. Mistryukov and V. F. Kucherov

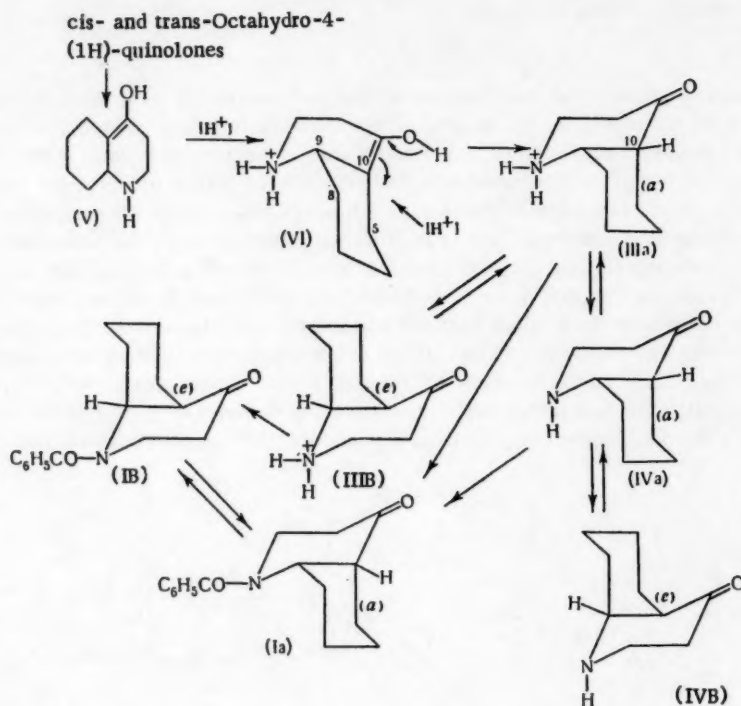
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,  
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In a previous communication [1] we described the synthesis of 1-benzoyloctahydro-4(1H)-quinolone (II), m.p. 109°, which was found to be different from the analogous compound (I), m.p. 145°, which had been prepared previously [2]. Although the original benzamide (I) was prepared from the base of octahydro-4(1H)-quinolone (IV), whereas the isomeric benzamide (II) was prepared from its hydrochloride (III), it did not seem very likely that the base and the hydrochloride of the same ketone would have different configurations with respect to the ring fusion. By the action of hydrogen chloride on the base (IV) under different conditions or by the acid hydrolysis of the benzamides (I) or (II), only one hydrochloride (III) was obtained. In the mother liquors remaining after the separation of (III) no sign of the presence of a second isomeric hydrochloride were found. In the benzoylation of (III) or (IV) with benzoyl chloride in pyridine in the cold we obtained one and the same benzamide (I). Isomerization under such mild conditions with the conversion of (IV) into (III) does not appear very likely. Final confirmation of this view was obtained from the results on the reduction of (III) and (IV) (see below). As the benzamide (I), corresponding to the hydrochloride (III) or the base (IV), readily isomerizes into the benzamide (II), it follows that there is ring-fusion isomerism between the most stable forms (III) and (IV) and the N-benzoyl derivative (II).



Hence, in the hydrochloride (III) some factor or other leads to the stability of only one type of ring fusion. Moreover, this type of ring fusion is found to be less stable and prone to isomerization when we pass to the N-benzoyl derivatives. It is evident that this factor determining the stable type of isomer is the ammonium group in the hydrochloride (III). The same factor determines also the steric structure of the base (IV). Actually, it may be supposed that

the isomerization of *cis*- and *trans*-(IV) proceeds through the intermediate formation of the enol form (V), which is common to the *cis*- and *trans*-forms and which under the attack of a proton donor will react at the most nucleophilic part of the molecule, the nitrogen atom. Hence, in this case also, the stage determining the steric structure will be the ketonization of the cation of the enol (VI). In the ketonization of the cation (VI) under the attack of the proton donor at C-10, apart from steric factors (cf. [3]) there must be an enormous effect due to electrostatic repulsion. It may therefore be expected that the protonization of the cation (VI) will occur on the side of the molecule most remote from the ammonium nitrogen, i.e. the incoming hydrogen will take up an equatorial position, which is equivalent to the formation of a *cis*-octahydro-4(1H)-quinolone cation. Also, this protonization reaction may be regarded as the reverse of the Hofmann cleavage of  $\beta$ -amino ketones, i.e., there is a common transition state for the direct and reverse reactions in which the bonds C<sub>9</sub>-N and C<sub>10</sub>-H occupy a *trans*-coplanar position. As can be seen from the scheme given below, such an arrangement of these bonds occurs in *cis*-octahydro-4(1H)-quinolone (IIIa). Hence, the predominance of the thermodynamically less stable isomer (III and IV) may be explained by the "kinetic factor" [3].

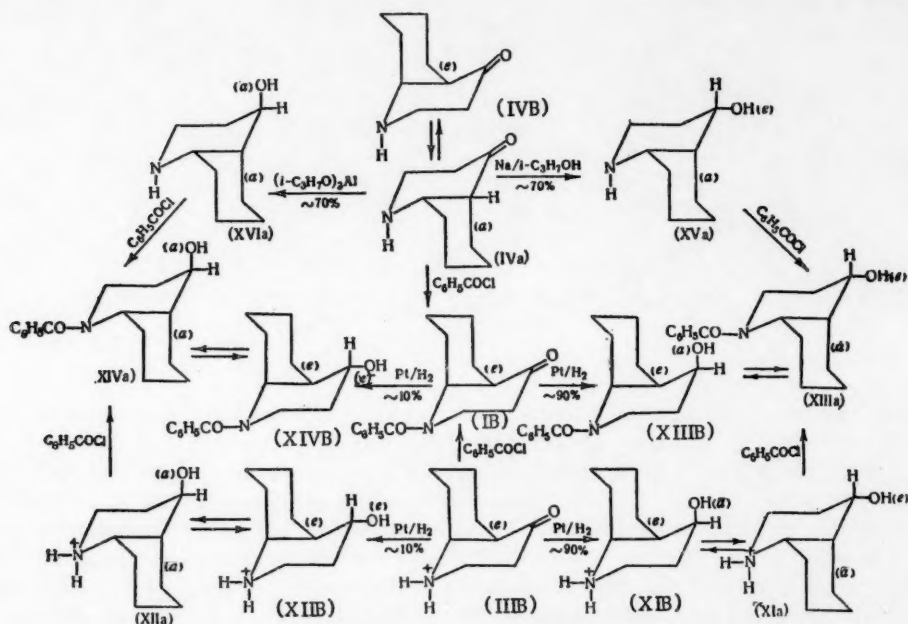


With the benzylation of octahydro-4(1H)-quinolone (IV), the basic properties of the nitrogen function are neutralized and, in the benzamide (I) formed, steric factors acquire a determining significance: the *cis*-isomer is readily isomerized into the thermodynamically more stable *trans*-isomer of 1-benzoyloctahydro-4(1H)-quinolone (II).

By stereospecific reduction via the desulfurization of the thioacetals (VII) and (VIII) we succeeded in passing from the benzamide (I) to the 1-benzoyldecahydroquinoline (IX), m.p. 56°, and from the isomeric benzamide (II) we obtained the corresponding 1-benzoyldecahydroquinoline (X), m.p. 99°. On the basis of the above considerations, these isomers should have *cis*- and *trans*-fusion of the rings, respectively. However, on the basis of the Auwers-Skita rule, the opposite configurations have been attributed to these isomers [4]. On the basis of such configurations it is impossible to explain the ready isomerization of the benzamide (I) into the benzamide (II), so that it appears to be necessary to reexamine previous conclusions regarding the steric structures of the isomeric 1-benzoyldecahydroquinolines and to take the view that the isomer (IX) of m.p. 56° is, in fact, the *cis*-isomer and that the isomer (X) of m.p. 99° has the *trans* configuration, as assumed in the present paper.

The anomalous stability of the *cis*-isomer of octahydro-4(1H)-quinolone (IV) and of its hydrochloride (II) is confirmed also by experiments on the reduction of this ketone. By the catalytic reduction of the hydrochloride (III) over platinum in water or in aqueous acetic acid we obtained a mixture of two isomeric hydrochlorides of decahydro-4-quinolinol with a predominance (above 90%) of the isomer of m.p. 275° (XI). The other isomer (XII), obtained in a smaller amount, melted at 230°. By the benzylation of these amino alcohols we obtained 1-benzoyldecahydro-4-quinolinols of m.p. 104° (XIII) and m.p. 140° (XIV). The same alcohols (XIII) and (XIV) were obtained by the hydrogenation of 1-benzoyloctahydro-4(1H)-quinolone (I), m.p. 145°, in aqueous dioxane. On hydrogenation in methanol we obtained a more complex mixture of reduction products containing also alcohols of the other series (with respect to ring fusion). The formation of such a proportion of isomers in the hydrogenation of decahydro-4-quinolinol hydrochloride indicates that the conversion of the amino group into ammonium has no substantial effect on the stereochemistry of the hydrogenation process and that in both cases the determining factors are steric in nature and lead to the formation of the thermodynamically less stable axial isomers of the alcohols. On reduction of octahydro-4(1H)-quinolone base (IV) with sodium in isopropyl alcohol, the predominating product (about 70%) was the amino alcohol (XV), the hydrochloride (XI) or *N*-benzoate (XIII) which were predominant in the mixtures of isomers formed in the catalytic reduction of the ketones (III) and (I). The other isomer, *cis*-decahydro-4-quinolinol (XVI), was predominant (about 70%) in the reduction of the octahydro-4(1H)-quinolone base (IV) with aluminum isopropoxide at the boil for 2.5 hours (cf. [5]).

As stated above, it may be supposed that the catalytic hydrogenation of the ketones (I) and (III) leads to the formation, at least in the first place, of an axial hydroxyl. From this it follows that the reduction of the base (IV), on the one hand, and of the hydrochloride (III) or benzamide (I), on the other, arises from different conversion forms of these ketones. As will be found from an examination of models for octahydro-4(1H)-quinolone hydrochloride the preferred conformation will be (IIIb), because "meta-axial" interaction of the  $\overset{\text{H}}{\underset{|}{\text{N}}} - \text{H}$  and  $\text{C}_5 - \text{C}_{10}$  bonds must occur in the conformation (IIIa). From the above considerations the conformation (IVa) follows for the octahydro-4(1H)-quinolone base. It is possible that in the last case only the conformation (IVa), of the two forms of close energy (IVa) and (IVb) is assigned the axial position on the basis that such forms must readily associate intermolecularly or with the solvent. Hence, the apparent contradiction, i.e. that catalytic hydrogenation and reduction with sodium give predominantly the same isomer, may be explained on the view that, through each of these methods gives the alcohol isomer most characteristic of the method, these isomers are derived from different conversion forms of the ketone and are consequently identical, i.e. in the catalytic reduction of the hydrochloride (III) or the benzamide (I) there is initially formation of the axial isomer of the alcohol (XIb) or (XIIIb) arising from conversion forms of the

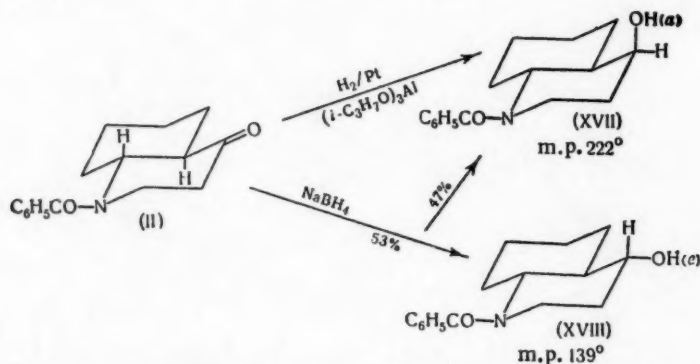


"meta-axial" interaction of the bonds  $C_4-O$  and  $C_9-C_8$ . Reduction with sodium in isopropyl alcohol also gives the most typical product for these conditions, the thermodynamically stable equatorial isomer (XVa), though this arises from the other conformation (a) of the ketone (IV). Analogously, on hydrogenation over nickel or reduction with aluminum isopropoxide the base (IV) gives a predominance of the alcohol (XVI), the *N*-benzoate (XIV) or hydrochloride (XII) which is formed in very small amounts in the catalytic reduction of (I) or (III). It follows from spectrum data (see below) that for the alcohol (XIV) the conversion form with an axial hydroxyl (XIVa) is the most favored form.

With the amide (I)  $NaBH_4$  gives a mixture of isomeric amino alcohols (XIII) and (XIV), the composition of which varies with the solvent [in aqueous methanol the proportions of (XIII) and (XIV) are about 3 : 2]. In the above considerations we did not examine the double boat or boat-chair conversion form for derivatives of *cis*-decahydro-quinoline, as this form probably makes no substantial contribution to the mixture of conversion isomer, which is confirmed by unsuccessful attempts to bring about the  $O \rightarrow N$  rearrangement of the *O*-acetates of the four isomeric decahydro-4-quinolins (see following communication). It is of interest to note the tendency of the alcohols (XIII) and (XIV) to give a molecular complex of m.p. 116.5-117.5° (proportions 1 : 1), which was taken erroneously in the first place to be one of the isomers of *cis*-1-benzoyldecahydro-4-quinolinol. However, the chromatography of even a single crystal on alumina on plates gave two spots, corresponding to the isomers (XIII) and (XIV).

From the reduction results it therefore follows that there is a single predominating conversion form (III) for the octahydro-4(1H)-quinolone and the benzamido ketone (I) which differs from the most stable conformation of the octahydro-4(1H)-quinolone base (IV). This difference in the predominating conversion forms of the base (IV) and the hydrochloride (III) may probably be explained by the more ready solvation of conformations of type (a) in the case of the free bases and of conformations of type (b) in the case of *cis*-decahydroquinoline derivatives having a heavy substituent on the nitrogen or with the amino group in the ammonium form. It is possible that in the case of free bases there is significant intermolecular interaction which comes least under the influence of steric factors when the interaction occurs between conformations of the (a) type. It is clear also that the data given on the reduction confirm the above-stated view on the absence of isomerization in the transition from octahydro-4(1H)-quinolone base to its hydrochloride and back or in benzylation under mild conditions.

The results on the reduction of the *trans*-ketone (II) form fairly unequivocal confirmation of its configuration. It was found that the catalytic hydrogenation of this benzamide over a platinum catalyst in dioxane or methanol solution gives mainly (about 80%) the same isomer (XVII) that is formed in 86% yield in reduction with aluminum isopropoxide. On the basis of its preparation and of chromatographic and spectrum data, the hydroxy group of this alcohol is assigned an axial position.



The other isomer of the alcohol, *trans*-1-benzoyldecahydro-4-quinolinol (XVIII), is formed in admixture with the isomer (XVII) on reduction of the ketone (II) with  $NaBH_4$ . The infrared spectra of the alcohols (XVII) and (XVIII) showed different absorptions in the  $C-O$  region. The alcohol (XVII) absorbs in the region of  $1041\text{ cm}^{-1}$  (axial hydroxyl), and the alcohol (XVIII) in the region of  $1052\text{ cm}^{-1}$  (equatorial hydroxyl), which confirms the structures assigned to these alcohols. Moreover, the spectrum data confirm the assignment of these alcohols to the *trans* series since, apart from the differences indicated, the spectrum of these compounds is analogous to that of the *trans*-1-benzoyldecahydro-quinolone (X) of m.p. 99°, particularly in the region of  $1027$  and  $1013\text{ cm}^{-1}$  ( $C-N$  bond, cf. [6]). The spectrum of *cis*-1-benzoyldecahydro-4-quinolinol (XIII) contains two lines at  $1050$  and  $1034\text{ cm}^{-1}$  of almost equal intensity, which corresponds to a mixture of conversion forms with equatorial and axial hydroxyls. The spectrum of the alcohol (XIV) shows only one band in the region of  $1025\text{ cm}^{-1}$  (axial hydroxyl, cf. [7]). Also, the alcohols (XIII) and (XIV) and *cis*-



1-benzoyldecahydroquinoline (IX), m.p. 56°, show characteristic absorption in the region of  $1010\text{ cm}^{-1}$  (1005, 1010, and  $1010\text{ cm}^{-1}$ , respectively).

#### EXPERIMENTAL

The chromatography, which we used as a check on the course of the reactions and for confirmation of the individuality of the isomers, was carried out on horizontal glass plates ( $13 \times 18\text{ cm}$ ) to which a layer of alumina, 0.5 mm in thickness, was applied. We used commercial alumina with an activity index of 2. The eluting mixture was applied with the aid of a vertical glass plate ( $4 \times 13\text{ cm}$ ) to which a strip of acetylated paper was fixed. To ensure constancy of results (moister alumina gives higher  $R_f$  values) during the application of test samples the plate was covered with a cover glass at a distance of 0.1-0.2 mm from the layer of alumina. The solvents used in the chromatography were first dried. In all the cases referred to below elution was carried out with a 1 : 1 mixture of benzene and acetone and the spots were developed with iodine vapor.

**1-Benzoyloctahydro-4(1H)-quinolone [(I)-cis].** This was prepared by the benzylation of octahydro-4(1H)-quinolone (III) with benzoyl chloride in pyridine [2] or by the benzylation of octahydro-4(1H)-quinolone (III) by the following method. Benzoyl chloride (3 ml; 10% excess) was added to a suspension of 4.5 g of the hydrochloride (III) in 20 ml of dry pyridine. As the mixture was stirred, its temperature rose and the hydrochloride dissolved rapidly. The mixture again became thick as a result of the precipitation of pyridine hydrochloride, and after 15 minutes it was stirred while water was added to a total volume of 100 ml; the crystals precipitated were filtered off, washed with water, and dried. We obtained 5.6 g (91%) of benzamide (I), m.p. 142.5-143.5°, raised by recrystallization from a mixture of ethyl acetate and hexane to 145° (the 2, 4-dinitrophenylhydrazone had m.p. 231-233°); there was no depression of melting point in admixture with the sample described previously [2].

**1-Benzoyloctahydro-4(1H)-quinolone [(II)-trans].** This was prepared as described previously [1] or by the isomerization of 1-benzoyloctahydro-4(1H)-quinolone (I) by the following methods:

a) To a suspension of 11 g of 1-benzoyloctahydro-4(1H)-quinolone in 22 ml of dioxane we added 9 ml of 4.8 N HCl in dioxane. The mixture was stirred until dissolution occurred, and was then left overnight at 20°. Solvent and HCl were driven off in a vacuum from a rotating evaporator at 20-24°; the residue was dissolved in 50 ml of benzene, 10 ml of water was added, and the aqueous layer was saturated with sodium carbonate. The benzene layer was filtered through a column of alumina (about 5 ml) and vacuum-evaporated. The oily residue was dissolved in a little ethyl acetate, and ether was added to the resulting solution. On standing, there separated 9.4 g of 1-benzoyloctahydro-4(1H)-quinolone (II), m.p. 109-110.5° and identical with the sample described previously.

b) A mixture of 2.57 g of the ketone (I) and a solution of 0.23 g of sodium in 20 ml of methanol was left at room temperature until solution was complete (three days). Methanol was driven off at 20°, and 25 ml of water and 75 ml of ether were added to the residue; the ether extract was vacuum-evaporated, and the residue was dissolved in a 1 : 3 mixture of benzene and heptane; the warmed solution was filtered through a layer of alumina and evaporated to dryness. Crystallization of the residue (2.54 g) from benzene-ether gave 1.66 g (65%) of 1-benzoyloctahydro-4(1H)-quinolone (II), m.p. 109.5-110°.

**Hydrolysis of 1-Benzoyloctahydro-4(1H)-quinolone [(II)-trans].** Water (1 ml) and acetic acid (3 ml) were added to a solution of 0.75 g of 1-benzoyloctahydro-4(1H)-quinolone (II) in 3 ml of concentrated HCl, and the mixture was boiled for eight hours. We obtained 0.24 g of octahydro-4(1H)-quinolone hydrochloride (III), m.p. 219-221°, undepressed by admixture of a known sample [1]. Analogous results were obtained on hydrolysis of 1-benzoyloctahydro-4(1H)-quinolone (I).

**trans-1-Benzoyloctahydro-4(1H)-quinolone Ethylene Thioacetal (VIII).** Boron trifluoride etherate (2 ml) was added to a solution of 0.8 g of 1-benzoyloctahydro-4(1H)-quinolone [(II)-trans] in 10 ml of glacial acetic acid and 1.6 ml of ethanedithiol; the reaction mixture was left overnight at 15° and then poured into water (about 70 ml); the organic reaction products were extracted with ether. We obtained 0.62 g of the ethylene thioacetal (VIII), m.p. 115-118°, raised by recrystallization from a mixture of ethyl acetate and hexane to 121.5-123° (0.35 g). Found: C 64.98; H 6.77; N 4.35; S 19.15%.  $\text{C}_{18}\text{H}_{23}\text{NOS}_2$ . Calculated: C 64.80; H 6.91; N 4.21; S 19.20%.

**cis-1-Benzoyloctahydro-4(1H)-quinolone Ethylene Thioacetal (VII).** By the above-described method, from 0.6 g of 1-benzoyloctahydro-4(1H)-quinolone [(I)-cis] we prepared an oily ethylene thioacetal (VII), which was used without further purification for the next reaction.

trans-1-Benzoyldecahydroquinoline (X). A solution of 0.24 g of the ethylene thioacetal (VIII) in 40 ml of dioxane was boiled with 4.5 g of Raney nickel for eight hours. We obtained 0.14 g of the benzoate (X), m.p. 93-96°, which, after being washed with isopentane, melted at 99-100° and showed no depression of melting point with a specially prepared [8] sample, described earlier as the *cis*-isomer [4].

cis-1-Benzoyldecahydroquinoline (IX). The unpurified liquid ethylene thioacetal (VII) prepared from 0.6 g of *cis*-1-Benzoyloctahydro-4(1H)-quinolone (I) was desulfurized as described above, and we obtained 0.25 g of *cis*-1-benzoyldecahydroquinoline (IX), m.p. 54-56°, undepressed by admixture of the sample described earlier as the *trans*-isomer [4].

Catalytic Hydrogenation of Octahydro-4(1H)-quinolone Hydrochloride (III). Octahydro-4(1H)-quinolone hydrochloride (III) (8.73 g) was exhaustively hydrogenated as a solution in water (30 ml) over platinum oxide at atmospheric pressure. Crystallization from a mixture of 24 ml of alcohol and 100 ml of ethyl acetate gave 7.06 g (80%) of decahydro-4-quinolinol hydrochloride (XI), m.p. 274.5-276°. Found: C 56.55; H 9.30; N 7.43; Cl 18.41%.  $C_9H_{18}NOCl$ . Calculated: C 56.40; H 9.40; N 7.31; Cl 18.50%. The hydrochloride obtained from the mother solutions (m.p. 226-230°) was benzoylated without purification (see below), and the mixture of benzoates was subjected to chromatography. The resulting chromatogram showed the presence in the mixture of about 60% of the benzamide (XIII) and about 40% of the isomeric benzamide.

1-Benzoyldecahydro-4-quinolinol (XIII). a) To a solution of 1.88 g of decahydro-4-quinolinol hydrochloride (XI) in 10 ml of water and 10 ml of dioxane we added 1.08 g of KOH; benzoyl chloride (1.16 ml) was added gradually to this mixture with stirring and cooling with ice; the reaction mixture was stirred for one hour, and dioxane and part of the water were driven off in a rotating evaporator. The usual treatment and crystallization from ethyl acetate and hexane gave 1.6 g of *cis*-1-benzoyldecahydro-4-quinolinol (XIII), m.p. 104-104.5°. Found: C 74.19; H 8.37; N 5.51%.  $C_{16}H_{21}NO_2$ . Calculated: C 74.13; H 8.12; N 5.41%;  $R_f$  0.41.

b) *cis*-1-Benzoyloctahydro-4(1H)-quinolone (I) (0.18 g) was hydrogenated as a solution in dry dioxane (5 ml) over previously reduced platinum oxide (0.05 g). Chromatography of the reaction mixture on a plate of alumina showed that the mixture contained mainly the benzamide (XIII) ( $R_f$  0.40) and only a small amount (less than 5%) of the isomeric *cis*-1-benzoyldecahydro-4-quinolinol (XIV), see below ( $R_f$  0.22). Crystallization from a mixture of ethyl acetate and hexane gave 0.12 g of the benzamide (XIII), m.p. 100.5-102°, identical with the sample described above.

Decahydro-4-quinolinol (XV). A solution of 13.3 g of octahydro-4(1H)-quinolone (III) (prepared from 17 g of the hydrochloride (VI) in a mixture of 20 ml of toluene and 16 ml of dry isopropyl alcohol was added to a suspension of 6.5 g of sodium in 50 ml of toluene (under nitrogen). The reaction mixture was boiled and stirred for 2 hr 45 min (cf. [5]), after which 10 ml of isopropyl alcohol was added and boiling was continued for a further 30 minutes. On the next day water (30 ml) was added, the toluene extracts were vacuum-evaporated, and the residue was crystallized from a mixture of toluene and hexane. We obtained 8.16 g (60%) of *cis*-decahydro-4-quinolinol (XV), m.p. 124-130°, the hydrochloride of which melted at 273-275° and showed no depression of melting point in mixture with the sample of (XI) prepared by the hydrogenation of octahydro-4(1H)-quinolone hydrochloride (III). The mother solutions were benzoylated with 3.1 ml of benzoyl chloride in 25 ml of dioxane and 25 ml of water in presence of 1.5 g of KOH, and from the mixture of benzoates we isolated 1.68 g (7.5%) of *trans*-1-benzoyldecahydro-4-quinolinol (XVII), m.p. 220° and 0.57 g of molecular complex of the alcohols (XIII) and (XIV) m.p. 116-117°, which is equivalent to a further amount of 1.25% of the isomer (XIII). On the basis of chromatographic data it could be considered that the residue contained about 20% of (XIII) and about 60% of (XIV).

Decahydro-4-quinolinol (XVI). To a solution of 0.92 g of octahydro-4(1H)-quinolone (IV) in 20 ml of isopropyl alcohol we added 2.4 g of aluminum isopropoxide, and the reaction mixture was stirred and boiled for 2 hr 45 min [5]; after conversion of the reaction products into the hydrochloride we obtained 0.81 g of decahydro-4-quinolinol hydrochloride (XII), m.p. 230.5-231° (total yield 70.5%). Found: C 56.57; H 8.67; N 6.07; Cl 15.39%.  $C_{11}H_{20}NO_2Cl$ . Calculated: C 56.53; H 8.57; N 6.0; Cl 15.20%. The base (XVI) isolated from the hydrochloride (XII) had m.p. 170-171° (from methanol).

cis-1-Benzoyldecahydro-4-quinolinol (XIV). Decahydro-4-quinolinol hydrochloride (XII) was benzoylated as indicated above and gave *cis*-1-benzoyldecahydro-4-quinolinol (XIV), m.p. 138.5-140° (from ethyl acetate-hexane). Found: C 73.69; H 8.07; N 5.45%.  $C_{16}H_{21}NO_2$ . Calculated: C 74.13; H 8.12; N 5.41%.

trans-1-Benzoyldecahydro-4-quinolinol (XVII). a) *trans*-1-Benzoyloctahydro-4(1H)-quinolone (0.13 g; m.p. 109-110.5°) was hydrogenated as a solution in 11 g of dry dioxane over a platinum catalyst. We obtained 0.10 g

(77%) of trans-1-benzoyldecahydro-4-quinolinol (XVII), m.p. 220.5-222°, raised by crystallization from alcohol to 222.5-223.5°. Found: C 73.70; H 8.04; N 5.39%.  $C_{16}H_{21}NO_2$ . Calculated: C 74.13; H 8.12; N 5.41%. Chromatography of the mother solution on alumina showed that the hydrogenation did not go to completion and that the mixture contained a little of the original ketone [(II)  $R_f$  0.79] (intense spot in 1 : 1 benzene-acetone), of the alcohol (XVIII)  $R_f$  0.35) and of the alcohol (XVII) ( $R_f$  0.55).

b) Octahydro-4(1H)-quinolone (II) (2.57 g; m.p. 109-110.5°) was added to a solution of 4.08 g of aluminum isopropoxide in 30 ml of dry isopropyl alcohol, and the solution was boiled for 2.5 hours. After crystallization of the reaction product from alcohol we obtained 2.24 g (86.5%) of trans-1-benzoyldecahydro-4-quinolinol (XVII), m.p. 222.5-223.5°, identical with the sample prepared as above. Chromatography of the mother solutions after separation of the main isomer showed the presence of the alcohol (XVIII) ( $R_f$  0.57) (intense spot), of the alcohol (XVIII) ( $R_f$  0.58) (spot of medium intensity), and of the original ketone ( $R_f$  0.79) (intense spot)\*. On the basis of this chromatogram the content of the alcohol isomer (XVIII) in the original mixture of isomers may be estimated to be about 5%, and that of the original ketone (II) to be about 5%.

trans-1-Benzoyldecahydro-4-quinolinol (XVIII). To a solution of 2.4 g of 1-benzoyloctahydro-4(1H)-quinolone (II) in 20 ml of methanol we added a solution of 0.5 g of  $NaBH_4$  in 5 ml of 0.1 N NaOH and 5 ml of methanol, and the mixture was stirred under water cooling; after 50 minutes it was acidified with acetic acid. Crystallization from alcohol gave 1.13 g (47%) of the alcohol (XVII), m.p. 222.5-223.5°, which was identical with the above-described sample, and from the mother solutions, after crystallization from a mixture of ethyl acetate and hexane, we obtained 1.28 g (53%) of trans-1-benzoyldecahydro-4-quinolinol (XVIII), m.p. 139.5-140.5° ( $R_f$  0.35). Found: C 73.88; H 8.20; N 5.62%.  $C_{16}H_{21}NO_2$ . Calculated: C 74.13; H 8.12; N 5.41%. The alcohol (XVIII) gave a sharp depression of melting point in admixture with a sample of the alcohol (XIV).

Hydrogenation of Octahydro-4(1H)-quinolone (IV) over Nickel. Octahydro-4(1H)-quinolone (IV) was hydrogenated as a solution in 50 ml of methanol over 5 g of Raney nickel at 50° with an initial pressure of 50 atm. Hydrogenation was rapid and was complete in one hour. Crystallization from ethyl acetate-hexane gave 8.3 g of decahydro-4-quinolinol (XVI), m.p. 170-171°. Found: C 69.41; H 10.60; N 8.65%.  $C_9H_{17}NO$ . Calculated: C 69.70; H 10.96; N 9.03%. The hydrochloride of this amino alcohol had m.p. 229-231.5°, undepressed by admixture of the sample described above (XII). Investigation of the chromatograms of the mother solutions remaining after the separation of the main amount of (XVI) showed that they contained approximately equal amounts of the amino alcohols (XV) and (XVI) together with a certain amount of other isomeric amino alcohols of the trans series.

The spectrographic part of the investigation was carried out by G. M. Kogan, to whom the authors express their thanks.

#### SUMMARY

1. On the basis of an investigation of the transformations of octahydro-4(1H)-quinolone it was shown that the most stable forms of the base and of the hydrochloride, on the one hand, and of the N-benzoyl derivative of this ketone, on the other, are isomers with respect to the manner of fusion of the rings.

2. It is concluded that the stereochemical characterization of cis- and trans-decahydroquinolines must be re-examined.

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\* The obvious errors in this sentence are present in the original Russian. - Publisher



# STEREOCHEMISTRY OF HETEROCYCLIC COMPOUNDS

## COMMUNICATION 8. DEBENZOYLATION AND STEREOCHEMISTRY OF DECAHYDROQUINOLINE AND ITS DERIVATIVES

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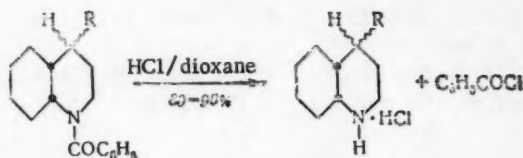
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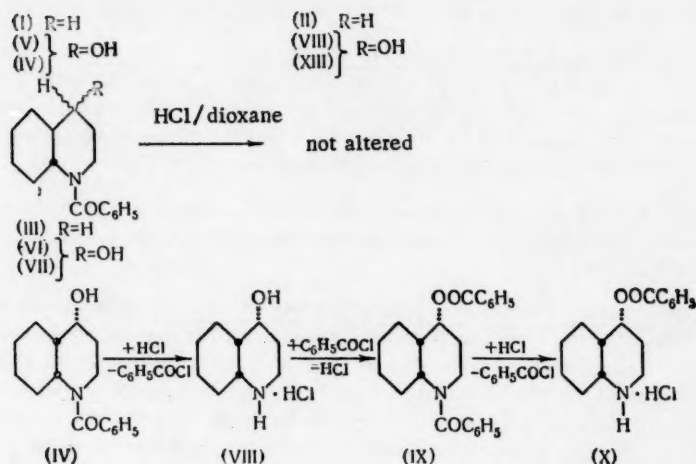
Original article submitted February 25, 1961

One of the widely used methods for the preparation of O-esters of amino alcohols and for the establishment of their steric structure is the method of N→O acyl migration, which occurs under the action of hydrogen chloride. It has been suggested that this reaction proceeds intramolecularly [1] via the intermediate formation of cyclic products of the hemiketal type [2]. In the present paper we describe another possible scheme for N→O migration under the action of hydrogen chloride in dioxane. Here the benzamides are split to benzoyl chloride and the amino alcohol hydrochloride, which may give the hydrochloride of the O-ester on subsequent intermolecular reaction. The reaction of hydrogen chloride with benzamides was found to be a stereospecific reaction that was greatly dependent on the steric structure of the original amide. Thus, *cis*- and *trans*-1-benzoyldecahydroquinolines [3] differ sharply in the character of their reaction with dry hydrogen chloride. When *cis*-1-benzoyldecahydroquinoline\* (I) is heated with a dioxane solution of hydrogen chloride, it is rapidly split up with formation in about 75% yield of *cis*-decahydroquinoline hydrochloride (II) and benzoyl chloride, whereas under these conditions *trans*-1-benzoyldecahydroquinoline (III) does not change. The same regularities are observed in the case of the isomeric 1-benzoyldecahydro-4-quinolins, and they were applied in the proof of the configuration of these compounds with respect to the fusion of the rings.

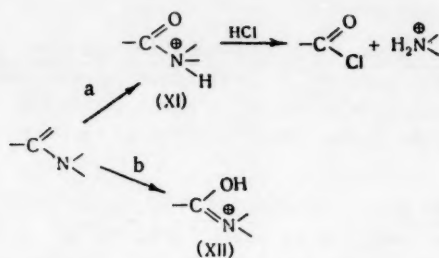
In the preceding communication [3] we described the synthesis of four isomeric 1-benzoyldecahydro-4-quinolins having melting points of 104° (IV), 140° (V), 139° (VI), and 222° (VII). Of these isomers, only the benzamides (IV) and (V) were split by hydrogen chloride to give high yields of the hydrochlorides of the corresponding bases and benzoyl chloride. On the other hand, under these conditions the alcohols (VI) and (VII) were not affected; their partial cleavage is observed only after prolonged heating. These results confirm the conclusion reached earlier [3] concerning the assignment of the alcohols (IV) and (V) to the *cis*-decahydroquinoline series. Moreover, the above-indicated cleavage reaction of amides with regeneration of the hydrochloride of the original base is useful for synthesis purposes. It is known that for the synthesis of the O-esters of amino alcohols either the N→O rearrangement of readily accessible amides of these amino alcohols [4, 5] or esterification by heating the amino alcohol hydrochloride with the acid chloride [4] has been used. In the case of alcohols difficult to esterify, e.g. decahydro-4-quinolinol hydrochloride (VIII), m.p. 275° [3], neither method was found to be suitable, for, when (VII) is heated with benzoyl chloride, either reaction does not go at all (at low temperature) or it leads to the formation of the N, O-dibenzoate (IX). There are no data in the literature on the selective removal of an N-benzoyl group. Moreover, as already stated N-acyl derivatives of decahydro-4-quinolins do not undergo rearrangement into O-esters (see also the following communication). We have shown that, when the N, O-dibenzoate (IX) is heated with hydrogen chloride in dioxane, selective elimination of the N-benzoyl group alone occurs with formation in good yield of the hydrochloride of the O-benzoyl derivative of decahydro-4-quinolinol (X).



\*The *cis*- and *trans*-decahydroquinolines are so named in accordance with the characterization given in the preceding paper.



Thus, the above-described results show that the character of the reaction of amides with anhydrous hydrogen chloride is determined to a considerable extent by steric factors. It is clear that an intermediate stage in the splitting of amides to the hydrochloride and the acid chloride is that of the protonization of the nitrogen atom (XI) in the amide. Another probable type of protonization of the amide group consists in the protonization of the oxygen function of the amide (XII) (cf. [6]).



The role of steric factors appears to amount to protonization along the route (a) in the case of amides that can be split and along (b) in the case of amides that cannot. However, it is at present still impossible to predict unequivocally which structural elements of decahydroquinoline determine protonization along one of these directions. We investigated also the action of hydrogen chloride on 1-benzoylpiperidine, as a model compound having a structure analogous to the heterocyclic part of the trans-1-benzoyldecahydroquinoline molecule. It was found that under the above-described conditions this compound scarcely undergoes any change (yield of hydrochloride about 10%), which forms further confirmation of the previously advanced view [3] of the structures of cis- and trans-decahydroquinolines.

#### EXPERIMENTAL

**Cleavage of cis-1-Benzoyldecahydroquinoline (I).** A solution of 2.32 g of cis-1-benzoyldecahydroquinoline [3], m.p. 104°, in 30 ml of dry dioxane was saturated with dry hydrogen chloride; the resulting solution was left for 30 minutes at 20° and then boiled for about 30 minutes. When the excess of hydrogen chloride had been driven off, the reaction mixture thickened as a result of the precipitation of crystals. On the next day dioxane was evaporated off on a rotary evaporator (temperature not above 25° with a vacuum of 25-30 mm); the residue was transferred to a filter



and washed with 25 ml of ethyl acetate. We obtained 1.25 g (75%) of cis-decahydroquinoline hydrochloride (II), m.p. 288-289° and identical with a known sample [7]. The mother solutions were vacuum-evaporated, and the residue was dissolved in 20 ml of isopentane (insoluble impurities were separated by filtration); to the resulting solution we added 3 ml of cyclohexylamine, and the reaction mixture, which had thickened as a result of the precipitation of crystals, was stirred for 30 minutes. Solvent was removed in a vacuum in a rotary evaporator; the dry residue was extracted with water and filtered off. Drying gave 1.41 g (74%) of N-benzoylcyclohexylamine, m. p. 146-147°.

Action of Hydrogen Chloride on trans-1-Benzoyldecahydro-quinoline (III). A solution of 1.13 g of trans-1-benzoyldecahydroquinoline (m.p. 99° [3]) in 15 ml of dioxane was treated as in the preceding experiment. The residue remaining after the evaporation of the dioxane crystallized out completely. The crystals were transferred to a filter and washed with isopentane. We obtained 1.06 g of unchanged 1-benzoyldecahydroquinoline, m.p. 99°. A further 0.05 g of starting material can be isolated from the mother solutions.

Action of Hydrogen Chloride on 1-Benzoylpiperidine. Under the conditions of the preceding experiment, from 1.82 g of 1-benzoylpiperidine we obtained 0.10 g of piperidine hydrochloride and 1.27 g of unchanged 1-benzoylpiperidine.

Action of Hydrogen Chloride on cis-1-Benzoyldecahydro-4-quinolinol (IV). A solution of 1.32 g of cis-1-benzoyldecahydro-4-quinolinol (IV), m.p. 104°, in 30 ml of dioxane was treated as indicated above. After 20 minutes the reaction mixture had thickened on account of the precipitation of crystals. On the next day solvent was vacuum-distilled off in a rotary evaporator (bath temperature less than 30°); ethyl acetate (20 ml) was added to the residue, and the crystals were filtered off. We obtained 0.84 g (86%) of cis-decahydro-4-quinolinol hydrochloride (VIII), m.p. 273-275°, identical with the previously described sample [3]. From the mother solutions we prepared 0.81 g (78%) of N-benzoylcyclohexylamine.

Action of Hydrogen Chloride on cis-1-Benzoyldecahydro-4-quinolinol (V). A solution of 1.2 g of cis-1-benzoyldecahydro-4-quinolinol (V), m.p. 140°, in 27 ml of a 6.5 N solution of dry hydrogen chloride in dioxane was saturated with dry HCl (5-8 minutes), and the reaction mixture was boiled for 45 minutes. At the end of this time the reaction mixture became thick as a result of the precipitation of crystals. After treatment in the way indicated above we obtained 0.74 g (83%) of cis-decahydroquinolinol hydrochloride (XIII), m.p. 225-226°. After recrystallization from a mixture of 2-methoxyethanol and ethyl acetate this hydrochloride melted at 226.5-227.5° (0.65 g) and showed no depression of melting point in admixture with the previously described sample [3]. From the mother solutions we prepared 0.87 g (92%) of N-benzoylcyclohexylamine.

Action of Hydrogen Chloride on Trans-1-Benzoyldecahydro-4-quinolinol (VI). A solution of 0.40 g of trans-1-benzoyldecahydro-4-quinolinol (VI), m.p. 139°, in 10 ml of dioxane was saturated with dry hydrogen chloride and treated as indicated above. After crystallization from ethyl acetate-hexane we obtained 0.30 g (75%) of the original N-benzoate, m.p. 138-139.5°. From the mother solution a further 0.04 g of impure unchanged reactant can be isolated; m.p. about 125°.

Action of Hydrogen Chloride on trans-1-Benzoyldecahydro-4-quinolinol (VII). On treatment of the alcohol (VII), m.p. 222°, under the above-indicated conditions we obtained about 90% of unchanged reactant. Under more severe conditions the yield of cleavage product increased. A solution of 0.75 g of trans-1-benzoyl-4-quinolinol (VII) in 20 ml of dioxane was therefore saturated with dry hydrogen chloride (15 minutes); the solution was left at 20° for 20 hours and then boiled for four hours. We obtained 0.40 g (53%) of the original alcohol (VII), m.p. 222°. From the mother solution we obtained 0.18 g (30.6%) of N-benzoylcyclohexylamine, and from the water-soluble part of the reaction products we obtained 0.16 g (29%) of trans-decahydro-4-quinolinol hydrochloride, m.p. 261-262.5° (after recrystallization from alcohol - ethyl acetate). Found: C 56.52; H 9.50; Cl 18.39%.  $C_9H_{13}NOCl$ . Calculated: C 56.4; H 9.40; Cl 18.50%.

Preparation of cis-Decahydro-4-quinolinol O-Benzoyl Ester Hydrochloride (X). A suspension of 3.1 g of cis-decahydro-4-quinolinol hydrochloride (VIII), m.p. 275°m in 10 ml of benzoyl chloride was boiled for 20 minutes. After ten minutes the vigorous liberation of hydrogen chloride ceased, and the reaction mixture became homogeneous. After dilution with chloroform and removal of insoluble products by filtration, excess of benzoyl chloride was vacuum-distilled off in a rotary evaporator (vacuum, 1 mm); the residue, the dibenzoate (IX), was dissolved in 50 ml of dry dioxane, and the solution was saturated with HCl (20 minutes) and was left for one hour at 20°; it was then boiled until the excess of hydrogen chloride ceased to be liberated (40 minutes). Dioxane was distilled off in the rotary evaporator, and the crystals were transferred to a filter and washed with 50 ml of ethyl acetate. We obtained 3.50 g (69%) of cis-decahydro-4-quinolinol O-benzoyl ester hydrochloride (X), which, after recrystallization from a mixture

of 2-methoxyethanol and ethyl acetate, had m.p. 275-277°. Found: C 64.67; H 7.49; N 4.81; Cl 11.93%.  $C_{16}H_{22}NO_2Cl$ . Calculated: C 64.9; H 7.45; N 4.74; Cl 12.0%.

#### SUMMARY

1. A new method is proposed for the cleavage of N-benzoyl derivatives of the decahydroquinolinol series by the action of dry hydrogen chloride in dioxane, and it is shown that this method is stereospecific.

2. This method was used for the confirmation of the configurations of decahydro-4-quinolinol isomers and for the synthesis of O-esters of some amino alcohols.

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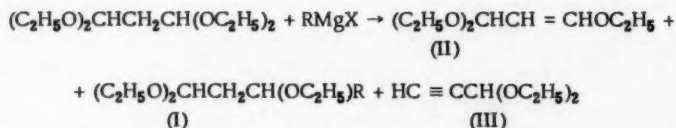
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COMMUNICATION 8. GRIGNARD REACTIONS WITH 1, 1, 3, 3-TETRAETHOXYPROPANE, 1, 1, 3, 5, 7, 7-HEXAETHOXYHEPTANE, AND 1, 1, 3, 5, 7, 9, 9-HEPTAETHOXYNONANE

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,  
No. 10, pp. 1830-1834, October, 1961  
Original article submitted February 21, 1961

$$\text{RCH}(\text{OC}_2\text{H}_5)_2 + \text{R}'\text{MgX} \rightarrow \text{RCH}(\text{OC}_2\text{H}_5)\text{R}'$$
$$\begin{array}{c} \text{R'MgX} \\ \text{(C}_2\text{H}_5\text{O)}_2\text{CHCH(R)CH(OC}_2\text{H}_5)_2 \xrightarrow{\quad\quad\quad} \\ \text{H}^+ \\ \text{(C}_2\text{H}_5\text{O)}_2\text{CHCH(R)CH(OC}_2\text{H}_5)_2\text{R}' \xrightarrow{\quad\quad\quad} \text{R}'\text{CH}=\text{C(R)CHO} \end{array}$$

It was found that all the Grignard reagents used reacted with 1, 1, 3, 3-tetraethoxypropane, but the normal reaction products (I) were formed in yields of only about 10-15%. The main reaction was the elimination of alcohol and the formation of 3-ethoxyacrolein diethyl acetal (II) in a yield of about 55-60%. We detected also the presence of small amounts of propionaldehyde acetal (III) in the reaction mixture. Hence, the over-all course of the reaction may be expressed as follows:



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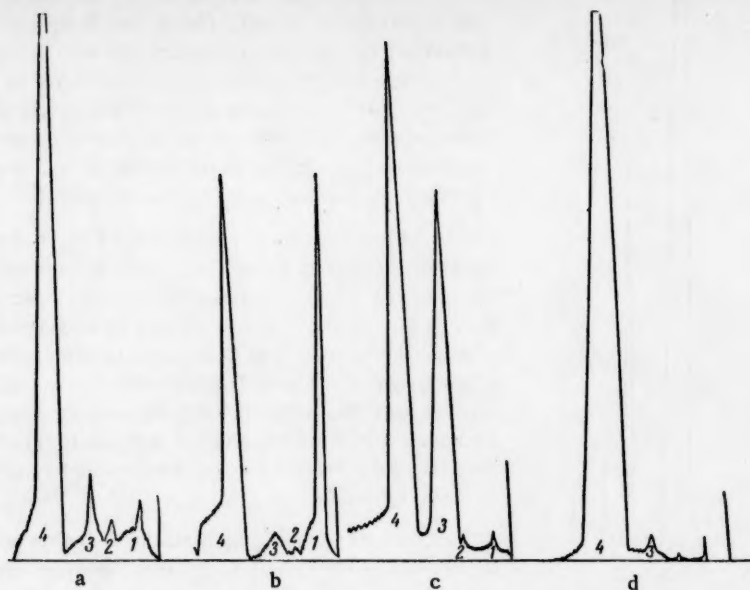
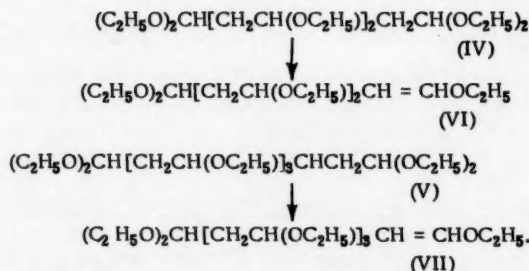


Fig. 1. Chromatograms: A) fraction of b.p. 115-119° (25 mm); B) ditto after the addition of propionaldehyde diethyl acetal; C) ditto after the addition of 3-ethoxyvaleraldehyde diethyl acetal; D) ditto after the addition of 3-ethoxyacrolein diethyl acetal.

The reaction between 1, 1, 3, 3-tetraethoxypropane and 3-methyl-3-buten-1-ynylmagnesium bromide led to the formation of two products: the first of these, the main product, had similar characteristics (boiling point and refractive index) to the mixture obtained in the reaction with ethylmagnesium bromide; in this product we found 3-ethoxyacrolein diethyl acetal (98% of the mixture) and propionaldehyde diethyl acetal (about 2% of the mixture) by means of gas-liquid chromatography (Fig. 2). According to elementary analysis, the second, higher-boiling fraction was 3-ethoxy-6-methyl-6-hepten-3-ynal diethyl acetal ( $I$ ;  $R' = C \equiv CC(CH_3) = CH_2$ ); the yield of this did not exceed 10-15%.

Analogous results were obtained in the study of the reaction of 1, 1, 3, 3-tetraethoxypropane with the Grignard reagent from dehydrolinalool. As a result of this reaction we isolated about 7% of product, which elementary analysis indicated to be 3-ethoxy-6-hydroxy-6, 9-dimethyl-9-undecen-4-ynal diethyl acetal ( $I$ ;  $R = C \equiv CCOH(CH_3)CH_2CH_2CH = C(CH_3)_2$ ). In this reaction the main product was again 3-ethoxyacrolein diethyl acetal with some admixture of a little propionaldehyde diethyl acetal.

Under the above-described conditions, 1, 1, 3, 5, 7, 7-hexaethoxyheptane (IV) and 1, 1, 3, 5, 7, 9, 9-heptaethoxynonane (V) reacted with ethylmagnesium bromide and again formed, according to elementary analysis, mainly products of the elimination of one alcohol group: 1, 3, 5, 7, 7-pentaethoxy-1-pentene (VI) and 1, 3, 5, 7, 9, 9-hexaethoxy-1-nonene (VII)





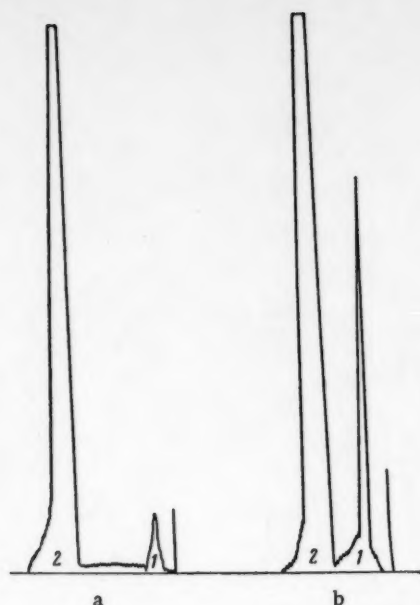
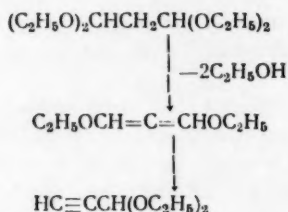


Fig. 2. Chromatograms: A) main fraction obtained in the reaction of 1, 1, 3, 3-tetraethoxypropane with 3-methyl 1-3-buten-1-ynylmagnesium bromide; B) ditto after the addition of propiolaldehyde diethyl acetal.

To confirm the structures of (VI) and (VII), their Raman spectra were determined\*. The spectra of both products contained a band at  $1598\text{ cm}^{-1}$ , characteristic for the  $\text{CH}=\text{CHOC}_2\text{H}_5$  group. It may therefore be considered to a fair degree of probability that (VI) and (VII) are indeed products formed by the elimination of one acetal ethoxy group. We did not succeed in checking the individual elimination products by the method of gas-liquid chromatography as they were retained firmly by the column which we used.

The elimination of alcohol from 1, 1, 3, 3-tetraethoxypropane under the conditions of the Grignard reaction cannot be explained by the catalytic effect of magnesium bromide. Special experiments showed that all the diacetals studied by us underwent scarcely any change when heated with magnesium bromide under the conditions of the Grignard reaction. It is probable that the ready elimination of alcohol under the action of Grignard reagents is a specific property of diacetals of this kind, and this reaction is appreciably quicker than the corresponding reaction proceeding by the scheme of the Grignard synthesis.

The formation of propiolaldehyde diethyl acetal may be represented as the result of the simultaneous elimination of two molecules of alcohol from a molecule of the original 1, 1, 3, 3-tetraethoxypropane via an allene system:



The formation of propiolaldehyde acetal may be represented also as occurring by the elimination of alcohol from 3-ethoxyacrolein diethyl acetal, but the amount of propiolaldehyde diethyl acetal formed is independent of reaction time, so that we considered the scheme given above to be the more probable.

#### EXPERIMENTAL

**Reaction of 1, 1, 3, 3-Tetraethoxypropane with Ethylmagnesium Bromide.** A solution of ethylmagnesium bromide (from 1.2 g of magnesium and 5.4 g of ethyl bromide) in 30 ml of dry ether was added dropwise to a solution of 11 g (0.05 mole) of 1, 1, 3, 3-tetraethoxypropane in 30 ml of ether with simultaneous removal of ether by distillation. For this purpose the temperature of the bath was gradually raised to the boil, and the mixture was heated for several hours (2-10). The reaction product was cooled, treated with ammonium chloride solution, and carefully extracted with ether. After two fractionations (after reaction had been carried on for 4-10 hours), we isolated about 5 g of fraction of b.p.  $115-119^\circ$  (25 mm) and  $n_D^{20}$  1.4220. A viscous brown residue (1.04 g) remained.

The main product was analyzed by the method of gas-liquid chromatography. A simple chromatograph with a thermal-conductivity detector [6] was used; the column was 2 m in length and 6 mm in diameter. The liquid stationary phase was a silicone oil applied to ground brick (particle diameter 0.25-0.5 mm). The mobile phase was hydrogen. The chromatography was carried out at  $120^\circ$ . The results of the analysis are given above.

**Reaction of 1, 1, 3, 3-Tetraethoxypropane with 3-Methyl-3-buten-1-ynylmagnesium Bromide.** The reaction was carried out in an analogous way with the same amounts of substances. After two fractionations of the reaction mixture we isolated 4.9 g of fraction of b.p.  $75^\circ$  (1 mm) and  $n_D^{21}$  1.4230 and 1.6 g of a fraction of b.p.  $90-93^\circ$  (1 mm)

\* The Raman spectra were determined by G. A. Kogan.



and  $n_D^{22}$  1.4498. The low-boiling fraction was investigated by means of gas-liquid chromatography. The higher-boiling fraction corresponded in analysis to 3-ethoxy-6-methyl-6-hepten-3-ynal. Found: C 70.00; 69.92; H 10.01; 9.96%.  $C_{14}H_{24}O_3$ . Calculated: C 69.96; H 10.07%.

Reaction of 1, 1, 3, 3-Tetraethoxypropane with the Grignard Reagent from Dehydrolinalool. The procedure was analogous to the above. From 11 g (0.05 mole) of 1, 1, 3, 3-tetraethoxypropane we obtained 9 g of a product which consisted of a mixture of 3-ethoxyacrolein diethyl acetal, propionaldehyde diethyl acetal, and unchanged dehydrolinalool. In addition we isolated 1.2 g of a product of b.p. 135-137° (1 mm) and  $n_D^{21}$  1.4580, which corresponded in analysis to 3-ethoxy-6-hydroxy-6, 9-dimethyl-9-undecen-4-ynal diethyl acetal. Found: C 69.94; 69.93; H 10.55; 10.50%.  $C_{19}H_{34}O_4$ . Calculated: C 69.90; H 10.50%.

Reaction of 1, 1, 3, 5, 7, 7-Hexaethoxyheptane with Ethylmagnesium Bromide. The procedure was as described above. From 9.1 g (0.025 mole) of 1, 1, 3, 5, 7, 7-hexaethoxyheptane, after two fractionations of the reaction mixture, we obtained 3.9 g of the product of the elimination of 1, 3, 5, 7, 7-pentaethoxy-1-heptene. Found: C 64.28; 64.37; H 11.17; 10.96%.  $C_{17}H_{34}O_5$ . Calculated: C 64.12; H 10.76%.

Reaction of 1, 1, 3, 5, 7, 9, 9-Heptaethoxynonane with Ethylmagnesium Bromide. The procedure was analogous to that described above. From 22.3 g (0.05 mole) of 1, 1, 3, 5, 7, 9, 9-heptaethoxynonane, after two fractionations of the reaction mixture, we obtained 10.58 g of a product of b.p. 160-164° (1 mm) and  $n_D^{17}$  1.4330, which corresponded in analysis to 1, 3, 5, 7, 9, 9-hexaethoxy-1-nonene. Found: C 64.48; 64.32; H 11.18; 11.04%.  $C_{21}H_{42}O_6$ . Calculated: C 64.58; H 10.84%.

In addition we obtained 8 g of a mixture of boiling range 166-195° (1 mm) and  $n_D^{17}$  1.4350; this was not investigated more closely.

#### SUMMARY

1. A study was made of the reactions of 1, 1, 3, 3-tetraethoxypropane, 1, 1, 3, 5, 7, 7-hexaethoxynonane with several Grignard reagents.
2. In all cases the main reaction was the elimination of alcohol and the formation, respectively, of 3-ethoxyacrolein, 1, 3, 5, 7, 7-pentaethoxy-1-heptene, and 1, 3, 5, 7, 9, 9-hexaethoxy-1-nonene.

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# PYRIDINE BASES DERIVED FROM 1-BUTEN-3-YNES

## COMMUNICATION 7. SYNTHESIS OF PYRIDINE BASES BY THE CONDENSATION OF 2-METHYL-1-BUTEN-3-YNE WITH KETONES AND AMMONIA

I. L. Kotlyarevskii and E. D. Vasil'eva

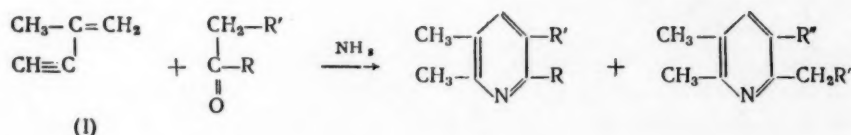
Institute of Chemistry, West Siberian Branch, Siberian Division  
Academy of Sciences, USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,  
No. 10, pp. 1834-1840, October, 1961

Original article submitted March 11, 1961

In a series of previous communications [1-5] we described a new method of synthesizing pyridine bases, which consisted in the condensation either of alcohols derived from 1-buten-3-yne or of 1-buten-3-yne and ketones with ammonia. In continuation of these investigations we have carried out work to determine the possibility of the synthesis of pyridine bases by this method with the use of substituted 1-buten-3-yne, instead of 1-buten-3-yne itself, which would considerably extend the possibilities of this method in synthesis and could be hoped to throw further light on the mechanism of this reaction.

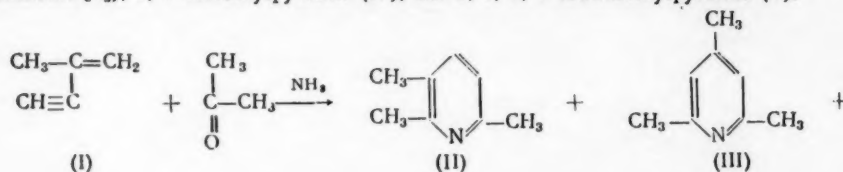
To determine the possibility in principle of introducing substituted 1-buten-3-yne into this reaction we investigated the condensation of 2-methyl-1-buten-3-yne (I) with various ketones. Experiment showed that 2-methyl-1-buten-3-yne will react with ketones and ammonia with formation of pyridine bases over a catalyst of the same composition [20 : 80  $\text{Cd}_3(\text{PO}_4)_2$  :  $\text{Al}_2\text{O}_3$ ] and under the same conditions as were previously found to be necessary for 1-buten-3-yne [2]. The catalyst was here prepared by a different method from that described in previous papers. The main reaction product formed in the condensation of 2-methyl-1-buten-3-yne (I) with ketones and ammonia corresponded to the mechanism by which the reaction of unsubstituted 1-buten-3-yne with ketones and ammonia was earlier found to proceed [2].

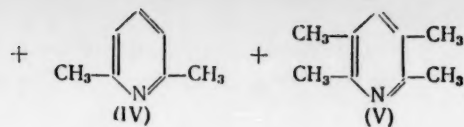


in which  $\text{R} = \text{CH}_2\text{R}''$ .

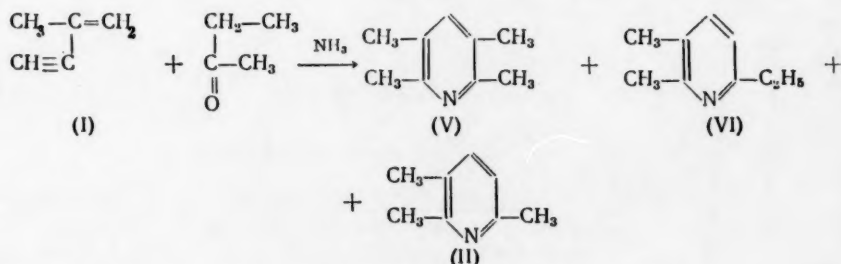
In the reaction of 2-methyl-1-buten-3-yne with ketones and ammonia somewhat more by-products were formed than in the reaction of the unsubstituted 1-buten-3-yne. Determining the causes of the formation of these by-products will probably form the subject of a special investigation.

The optimum conditions differed little from those found for 1-buten-3-yne. Under these conditions as main product from 2-methyl-1-buten-3-yne (I), ammonia, and acetone we obtained 2, 3, 6-trimethylpyridine (II), and there was simultaneous formation of 2, 4, 6-trimethylpyridine (III) (probably the result of direct condensation of acetone with ammonia [6]), 2, 6-dimethylpyridine (IV), and 2, 3, 5, 6-tetramethylpyridine (V).

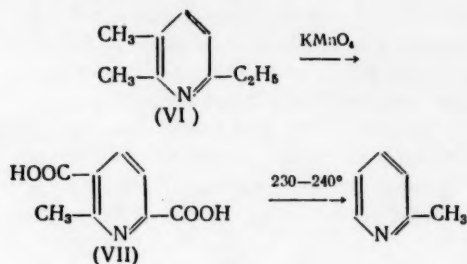




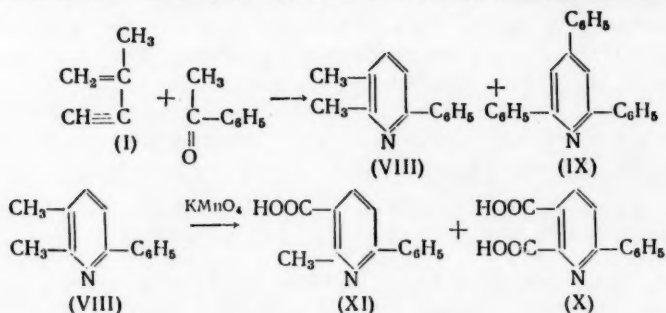
From 2-methyl-1-buten-3-yne (I) and butanone and ammonia two main products were formed: 2, 3, 5, 6-tetramethylpyridine (V) and 6-ethyl-2, 3-dimethylpyridine (VI). 2, 3, 6-Trimethylpyridine was found as a by-product.



The structure of 6-ethyl-2,3-dimethylpyridine (VI) needed further proof since there was some doubt about the pyridine (VI) described in the literature [7]; although the constants of the substance that we obtained were close to the values given in the literature, it was impossible to check further the identity of the substance because the authors who obtained (VI) for the first time gave no details of any derivatives. The structure of the pyridine (VI) was proved by its oxidation. By its oxidation the same dicarboxylic acid was formed as in the oxidation of the known 2, 3, 6-trimethylpyridine, which shows the distribution of the alkyl substituents in the nucleus. This acid [6-methyl-2, 5-pyridinedicarboxylic acid (VII)] contains an  $\alpha$ -carboxyl (color reaction with  $\text{FeSO}_4$ ) and on decarboxylation gives 2-picoline. The other possible pyridine that could give the acid (VII) (3-ethyl-2, 6-dimethylpyridine) did not correspond to the pyridine (VI) in its constants and the melting point of the picrate.



Acetophenone is analogous to acetone in its condensation with 2-methyl-1-buten-3-yne (I) and ammonia. The main product is 2, 3-dimethyl-6-phenylpyridine (VIII); a by-product is 2, 4, 6-triphenylpyridine (IX), formed by the direct condensation of acetophenone with ammonia [8]. The structure of the pyridine (VIII) was proved by its oxidation into the known 6-phenylpyridine-2, 3-dicarboxylic acid (X) and 2-methyl-6-phenylnicotinic acid (XI).



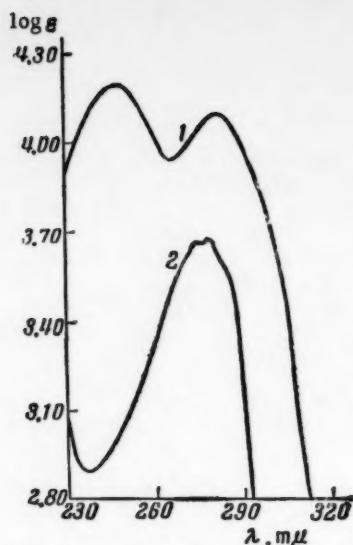
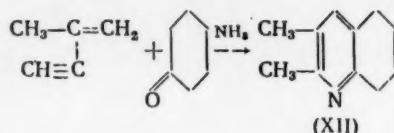


Fig. 1.

The condensation of 2-methyl-1-buten-3-yne (I) with cyclohexanone and ammonia gives the known 5, 6, 7, 8-tetrahydro-2, 3-dimethylquinoline (XII):



In fig. 1 we give the ultraviolet spectra of (VIII) and (XII).

#### EXPERIMENTAL

**Preparation of 2-Methyl-1-buten-3-yne.** The synthesis was carried out in a round-bottomed two-necked flask fitted with a reflux condenser connected to a condenser set for distillation followed by a trap cooled with ice and salt. The flask was charged with 250-300 ml of 30% sulfuric acid solution, and the water in the jacket of the reflux condenser was kept at 50-60° while 100-150 g of 2-methyl-2-butanol was added over a period of 2.5-3 hours to the boiling sulfuric acid. After distillation 2-methyl-1-buten-3-yne was obtained in 60-65% yield- b.p. 32-35° (720-730 mm). The literature [9] gives b.p. 31-34°.

**Preparation of the  $\text{Cd}_3(\text{PO}_4)_2 : \text{Al}_2\text{O}_3$  (20 : 80) catalyst.** Aluminum turnings (56 g) were added gradually to a solution of 90 g of sodium hydroxide in 1500 ml of water, and to the resulting sodium aluminate solution a solution of 130 g of ammonium carbonate in 1000 ml of water was added. The precipitate of aluminum hydroxide formed was washed carefully with distilled water until neutral to phenolphthalein. The moist cake of aluminum hydroxide, containing 79 g of aluminum oxide, was shaken with water, and to the suspension we added an aqueous solution of 35 g of cadmium nitrate tetrahydrate in such a way that the total volume of the suspension amounted to 1.5-2 liters. Then, with vigorous stirring we added a solution of triammonium phosphate in the amount necessary for the precipitation of cadmium phosphate. The resulting catalyst was filtered off, washed, and gently dried down at room temperature to give a viscous mass, which was molded into the form of little sausages, 3 mm in diameter, and dried in air for one day; the product was cut up into granules about 3-4 mm in length. These granules were roasted in a quartz catalysis tube in the following manner: the furnace temperature was raised to 100° in 15 minutes, to 150° in one hour, to 500° in 3.5 hours, and then kept at 500° for two hours. The catalyst (50 ml) did not lose its activity on passage of 30-35 g of 2-methyl-1-buten-3-yne together with the corresponding amounts of the various ketones, and it was readily regenerated by a two-hour roasting in air at 500-600°.

**Condensation of 2-Methyl-1-buten-3-yne (I) with Acetone and Ammonia.** All the condensation reactions were carried out in the usual flow apparatus, which was described previously [1, 2]. A mixture of 2-methyl-1-buten-3-yne and acetone at a molar ratio of 1 : 3 was passed at a space velocity of 1.15-1.30 hr<sup>-1</sup> through the catalysis tube heated at 390-400°. Ammonia was passed simultaneously at a rate of 29-30 liters/hr. As soon as the mixture of reactants was passed into the catalysis tube, the temperature in the catalyst rose spontaneously to 420-430° and remained at this level throughout the whole process. At the end of the catalysis the temperature fell again to 390-400°. The catalyzate obtained from 8 g of 2-methyl-1-buten-3-yne and the corresponding amount of acetone was dissolved in 100 ml of 1 : 1 hydrochloric acid; the neutral products were carefully extracted with ether, and the acid solution was made strongly alkaline with solid alkali; the base liberated was extracted with ether. After distillation we obtained 5.5-6 g of crude pyridines. Fractionation of 100 g of bases accumulated in this way through a column of 30-plate efficiency at atmospheric pressure gave the following pyridine bases:

1) 2, 3, 6-Trimethylpyridine, 51.6 g; b.p. 168° (724 mm);  $n_D^{20}$  1.5031; picrate, m.p. 148-148.5°; mixture with known sample, m.p. 148-148.5°. The literature [2] gives: b.p. 168-170°;  $n_D^{20}$  1.5030; picrate, m.p. 147°.

2) 2, 4, 6-Trimethylpyridine, 25.6 g; b.p. 166-167° (720 mm);  $n_D^{20}$  1.4980; picrate, m.p. 155-155.5°; mixture with known sample, m.p. 154-155.5°. The literature [2] gives: b.p. 170.5° (762 mm);  $n_D^{20}$  1.4983; picrate, m.p. 155-156°.



3) 3,2, 6-Dimethylpyridine, 18 g; b.p. 141° (730 mm);  $n_D^{20}$  1.4968; picrate, m.p. 162-162.5°; mixture test m.p. 162.162.5°. The literature [2] gives: b.p. 141-142°;  $n_D^{20}$  1.4968; picrate, m.p. 162-162.5°.

4) 2, 3, 5, 6-Tetramethylpyridine, 4 g; b.p. 195-196° (730 mm) picrate, m.p. 173.5-174°. The literature [10] gives: b.p. 197-198°; picrate, m.p. 173-174°.

Condensation of 2-Methyl-1-buten-3-yne (I) with Butanone and Ammonia. The condensation was carried out in the same apparatus and under the same conditions as in the preceding experiment. From every 8 g of 2-methyl-1-buten-3-yne and the corresponding amount of butanone we obtained 6.5-7 g of a mixture of pyridine bases. By fractionation through the 30-plate column 40 g of this mixture gave:

1) 2, 3, 5, 6-Tetramethylpyridine, 51%; b.p. 195-196° (730 mm); m.p. 79-80°; picrate, m.p. 173.5-174°.

2) 2, 3, 6-Trimethylpyridine, 11%; b.p. 168° (724 mm);  $n_D^{20}$  1.5031; picrate, m.p. 148-148.5°.

3) 6-Ethyl-2, 3-dimethylpyridine, 17%; b.p. 185.5-186.5° (730 mm);  $n_D^{20}$  1.4998; picrate, m.p. 126-126.5°. Found: N 15.47%.  $C_9H_{13}N$ .  $C_6H_5N_3O_7$ . Calculated: N 15.37%. Chloroplatinate, m.p. 195-196° (decomp.). The literature [7] gives: b.p. 190-190.5° (764 mm).  $n_D^{20}$  1.4970.

The following investigations were carried out to prove the structure of 6-ethyl-2, 3-dimethylpyridine (VI).

Oxidation of 6-ethyl-2, 3-dimethylpyridine. The pyridine (VI) (1.3 g) was stirred in a boiling water bath with a solution of 6 g of potassium permanganate in 250 ml of water; after 90 minutes the solution had been decolorized, and over a period of four hours 6.1 g of potassium permanganate was added in portions at 100°. After evaporation of the filtrate down to 50 ml and acidification to Congo Red with hydrochloric acid, there was a copious crystalline precipitate of 6-methyl-2, 5-pyridinedicarboxylic acid (VII), m.p. 231-232°, which gave a pink color with ferrous sulfate characteristic for 2-pyridinecarboxylic acids. Found: C 50.32; H 4.10; N 7.53%.  $C_8H_7NO_4 \cdot \frac{1}{2} H_2O$ . Calculated: C 50.53; H 4.24; N 7.36%. On titration of the acid in aqueous-alcoholic solution with potassium hydroxide to phenolphthalein we found: COOH 48.3%.  $C_8H_7NO_4 \cdot \frac{1}{2} H_2O$ . Calculated: COOH 47.3%.

Oxidation of 2, 3, 6-trimethylpyridine (II). Over a period of five hours, 21.5 g of potassium permanganate was added to a mixture of 2.72 g of the pyridine (II), 3 g of KOH, and 300 ml of water in a boiling water bath with stirring. When the solution was decolorized, it was filtered, and the filtrate was evaporated down to 50 ml and acidified to Congo Red with hydrochloric acid. There was a precipitate of the potassium salts of 6-methyl-2, 5-pyridinedicarboxylic acid (VII) and 2, 3, 6-pyridinetricarboxylic acid. The potassium salts were dissolved in water and precipitated as copper salts by the addition of cupric acetate solution; the precipitate was washed with hot water, suspended in 50 ml of water, treated with hydrogen sulfide, and filtered hot. After standing overnight the filtrate gave a precipitate of 400 mg of 6-methyl-2, 5-pyridinedicarboxylic acid (VII), m.p. 231-232°, along and in admixture with the sample obtained by the oxidation of 6-ethyl-2, 3-dimethylpyridine. The mother liquor was evaporated and gave 2.1 g of 2, 3, 6-pyridinetricarboxylic acid, which began to decompose at 140°, blackened at 180-200°, and melted at 226-227°. Found: COOH 65.5%.  $C_8H_5NO_6$ . Calculated COOH 63.9%. The tricarboxylic acid was very soluble in water and gave a bluish-red color with ferrous sulfate solution; its copper salt was blue with a pearly reflex.

Decarboxylation of 6-methyl-2, 5-pyridinedicarboxylic acid (VII). The acid (200 mg) was heated in a test tube in a metal bath. At 230° the substance suddenly melted and decomposed with the liberation of carbon dioxide; 2-picoline condensed in the upper part of the tube. Its picrate had m.p. 165.5-166.5°, alone and in admixture with a known sample.

Condensation of 2-Methyl-1-buten-3-yne (I) with Acetophenone and Ammonia. The condensation was carried out under the same conditions as in the previous case. From 8 g of 2-methyl-1-buten-3-yne and the corresponding amount of acetophenone we obtained 14-15 g of bases. Vacuum fractionation of 75 g of these bases gave the following pyridines:

1) 2,3-Dimethyl-6-phenylpyridine (VIII), 40%; b.p. 159-160° (9mm); b.p. 145.5° (1mm);  $n_D^{20}$  1.6075;  $d_4^{20}$  1.0487; picrate, m.p. 192-193°. Found: N 13.75%.  $C_{13}H_{13}N$ .  $C_6H_5O_7$ . Calculated: N 13.58%. The chloroplatinate had m.p. 208-209°.

2) 2, 4, 6-Triphenylpyridine (IX), 13%; m.p. 139.5-140°; picrate, m.p. 195-195.2°. The literature [11] gives: m.p. 138-139°; picrate, m.p. 193.5°.

To prove the structure of 2, 3-dimethyl-6-phenylpyridine (VIII) we carried out the following experiments: a) A hot solution of 12 g of potassium permanganate was added to 3.5 g of 2, 3-dimethyl-6-phenylpyridine (VIII) in



300 ml of water over a period of 16 hours. Stirring was continued at 100° until the solution was decolorized. To complete the decolorization a few drops of alcohol were added. The precipitate of manganese dioxide was filtered off and washed with hot water, the filtrate with the wash waters was acidified to litmus and evaporated down to 50 ml; after acidification to Congo Red an oil separated. Crystalline cupric acetate was added to the boiling aqueous emulsion of this oil until a greenish precipitate ceased to form. The precipitate was washed with water, suspended in 50 ml of water, and treated with hydrogen sulfide. The copper sulfide that separated was filtered off, and the filtrate was evaporated down to 5-10 ml; on cooling an oil was precipitated, and this crystallized out after several days. The acid, after being crystallized from aqueous alcohol, melted in the following way: from 133° to 135° it "bubbled" without melting, and it melted only at 227-230°; the literature [12] states m.p. 148-150° (decomp.). The acid was readily soluble in water and in alcohol; from aqueous alcohol it separated in the form of needles, which effloresced when dried. The reaction for 2-carboxyl with ferrous sulfate was positive. This acid is 6-phenyl-2,3-pyridinedicarboxylic acid(X). Found: C 64.09; H 3.62; COOH 36.6%.  $C_{13}H_9NO_4$ . Calculated: C 64.20; H 3.73; COOH 37.4%.

A little of the pure acid was heated in a test tube in a metal bath at 200° for 30 minutes. The acid was decarboxylated in the range 130-140°; the reaction product sublimed and melted at 230-233°. According to the literature [13] 6-phenylnicotinic acid has m.p. 232-233°.

b) 2, 3-Dimethyl-6-phenylpyridine (VIII) (3.5 g) was oxidized with one-half an equivalent of potassium permanganate (6.3 g); the filtrate was evaporated down to 100 ml and acidified with hydrochloric acid. There was a precipitate of 2-methyl-6-phenylnicotinic acid (XI) (1.2 g), and from the mother liquor we isolated 1.4 g of 6-phenyl-2, 3-pyridine-dicarboxylic acid (X). The acid (XI) gave no reaction with ferrous sulfate; it was poorly soluble in water, but readily in alcohol. After being crystallized from aqueous alcohol it melted at 193-193.5°. The literature gives: m.p. 196° [12]; m.p. 190° [14]. Found: C 73.54; H 5.05; N 6.73; COOH 20.57%,  $C_{13}H_{11}NO_2$ . Calculated: C 73.22; H 5.20; N 6.56; COOH 21.1%.

Condensation of 2-Methyl-1-buten-3-yne (I) with Cyclohexanone and Ammonia. By the condensation of 2-methyl-1-buten-3-yne (I) with cyclohexanone and ammonia we obtained 5, 6, 7, 8-tetrahydro-2, 3-dimethylquinoline (XII) in 22% yield calculated on the 2-methyl-1-buten-3-yne passed; m.p. 36-37°; b.p. 109-110° (1 mm); picrate (needles from alcohol), m.p. 172.8-173°. Found: N 14.34%.  $C_{11}H_{15}N$ .  $C_6H_5N_3O_7$ . Calculated: N 14.35%. Chloroplatinate, m.p. 196-197°. The literature [15] gives: b.p. 125-126° (14 mm); m.p. 38°; picrate, m.p. 169°. Apart from 5, 6, 7, 8-tetrahydro-2, 3-dimethylquinoline (XII), we obtained other high-boiling bases, which appeared to be products of the reaction of cyclohexanone with ammonia.

#### SUMMARY

1. It is shown that it is possible in principle to synthesize pyridine bases by the condensation of substituted 1-buten-3-yne (2-methyl-1-buten-3-yne) with ketones and ammonia over the catalyst  $Cd_3(PO_4)_2/Al_2O_3$ , which considerably widens the possibilities of the method in synthesis.

2. The nature of the main products confirms the correctness of the mechanism proposed for this condensation in the case of the reaction of ketones and ammonia with unsubstituted 1-buten-3-yne.

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## BUTADIYNE DERIVATIVES

COMMUNICATION 9. SYNTHESIS OF UNSATURATED ALKOXY AND ALKYLTHIO ACETALS HAVING C<sub>7</sub>-C<sub>15</sub> CARBON CHAINS IN THEIR MOLECULES

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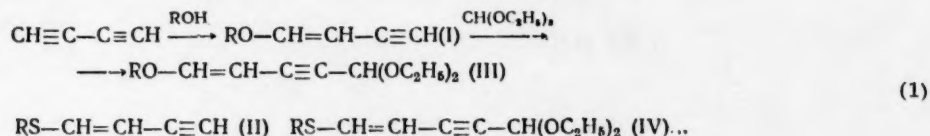
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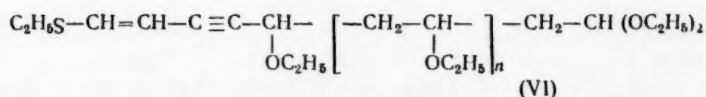
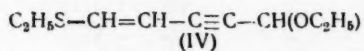
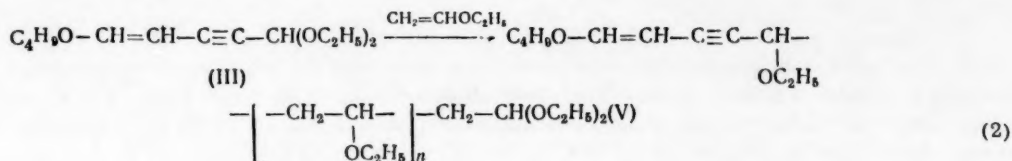
Original article submitted May 3, 1961

Syntheses based on butadiyne and alcohols or thiols which we studied previously [1,2] led to the preparation of various unsaturated ethers (I) and sulfides (II). By the reaction of the ethers obtained with triethyl orthoformate we succeeded [2,3] in introducing the acetal grouping into the molecules of these compounds and synthesizing various unsaturated ether acetals (III) and sulfide acetals (IV) in accordance with the scheme:



The object of the present work was to investigate the possibility of increasing the size of the carbon skeleton of butadiene derivatives by the addition of vinyl ethers and sulfides to the ether acetals and sulfide acetals so as to obtain compounds containing an enyne grouping. In the literature [4-10] the use of alkyl vinyl ethers to increase the size of the carbon skeletons of the molecules of certain acetals, ketals, and ortho esters is described. The use of alkyl vinyl sulfides in chain-lengthening reactions with acetals is not known in the literature. There is only a description of the addition of one or two molecules of ethyl vinyl ether to acetaldehyde diethyl mercaptal under the influence of  $\text{BF}_3$  [11].

The case that we have studied of the addition of vinyl ethers and vinyl sulfides to unsaturated ether acetals and sulfide acetals forms a new example of a telomerization reaction proceeding by an ionic mechanism, similar to the addition of vinyl ethers to acetaldehyde acetals [8-10]. The reaction of vinyl ethers with the unsaturated alkoxy and alkylthio acetals (III) and (IV) proceeds by Equation (2) and leads to the formation of mixtures of telomeric products containing carbon chains of  $C_{15}$  and higher:

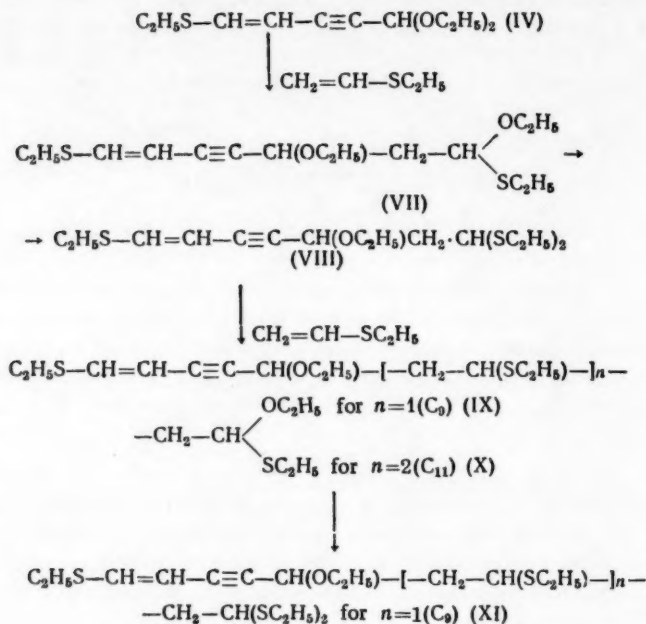


(Va)  $\underline{n} = 0$  ( $C_7$ ); (Vb)  $\underline{n} = 4$  ( $C_{15}$ ); (VIa)  $\underline{n} = 0$  ( $C_7$ ); (VIb)  $\underline{n} = 2$  ( $C_{11}$ ).

It is a characteristic feature of this reaction that, unlike the reaction of vinyl ethers with acetaldehyde acetals, the first molecule of vinyl ether adds more slowly than the second, which is probably associated with the lower mobility of the alkoxy group of the original acetal due to the effect of the neighboring triple bond. This probably explains the ease of formation of telomerization products.

In the reaction of ethyl vinyl ether with the butoxy acetal (Equation (2)), among individual products isolated was the product of the addition of one molecule of vinyl ether with a  $C_7$  carbon chain and a product of the addition of five molecules of vinyl ether ( $C_{15}$ ). Of products of the addition of the vinyl ether to the ethylthio acetal we isolated the products of the addition of one and of three molecules of vinyl ether with  $C_7$  and  $C_{11}$  carbon chains, respectively.

The use of alkyl vinyl sulfides in the chain-growth reaction is of considerable interest, for, apart from the increase in the size of the carbon skeleton of the acetal, this reaction makes it possible to introduce alkylthio groups into the molecule simultaneously. As a result, molecules may be obtained which contain  $n - 2$  sulfur-containing groups in a total number of  $n$  substituting groups. The reaction of ethyl vinyl sulfide with 5-(ethylthio)-4-penten-2-ynal diethyl acetal proceeds in accordance with the scheme (below) and leads to the formation of a mixture of telomeric products.



The mechanism of the successive additions of the vinyl sulfide to unsaturated sulfide acetals probably consists in the elimination of an alkoxy group of the acetal as an anion under the influence of the catalyst and the subsequent addition of it and of the cation formed to the vinyl sulfide molecule at the double bond. The mixed mercaptal then formed reacts in like fashion with the next molecule of vinyl sulfide etc., and as the ion responsible for the further process there figures the complex cation  $RS-CH=CH-C\equiv C-CH(OR)-[CH_2-CH(SR)]_nCH_2-\overset{+}{C}H-SR$ . The reaction may be terminated by the symmetrization of mixed mercaptals, which was proved by quantitative mercuric chloride titration of the terminal groups of the telomers. In view of the reduced mobility of the alkylthio group under ionic conditions, as has already been noted [3], it is difficult to imagine that the vinyl sulfide would add to the mercaptal under the conditions studied.

The telomeric products of the addition of ethyl vinyl sulfide to the sulfide acetal are readily disproportionating mixed mercaptals, whose isolation and purification are impossible by vacuum fractionation. Chromatography on alumina of fourth-grade activity was found to be effective. Of the mixed mercaptals we succeeded in isolating those with  $C_7$ ,  $C_9$ , and  $C_{11}$  chains, and of the full mercaptals -  $C_7$  and  $C_9$ . The structures of the products were proved by mercuric chloride titration and spectroscopically. The infrared spectra of the substances synthesized were determined on a double-beam spectrophotometer ( $UR = 10$ ). The pure substances were placed between sodium chloride plates;

the error in the determination of vibration frequency did not exceed  $\pm 5 \text{ cm}^{-1}$ . The intensities of the absorption bands were expressed on a ten-grade scale. From the spectra (Table 1) it is seen that in the compounds investigated the values of the frequencies for the vibrations of the C=C and C $\equiv$ C groups are lower than those for the same vibrations in molecules containing isolated C=C and C $\equiv$ C bonds. In Table 1, for comparison we give the vibration frequencies for double bonds in compounds of the type ROC=CR' and RC $\equiv$ CR', in which R and R' are aliphatic groups. Isolated double and triple bonds that are not at the ends of the chain generally give weak adsorption bands in the infrared spectra [12]; in the present case they are intense. The displacement of the frequencies and the increased intensity of the infrared absorption bands indicate the presence of conjugated multiple bonds in the compounds studied.

TABLE 1

Expt.	Formula	Vibration frequencies ( $\text{cm}^{-1}$ )		
		C $\equiv$ C	C=C	Other frequencies
1	$\text{C}_2\text{H}_5\text{S}-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CH}(\text{OC}_2\text{H}_5)_2$ (IV)	2208(3)	1562(3)	1019(9); 1060(10); 1087(9); 1140(9); 1278(5); 1330(8); 1356(8); 1445(5); 1465(5)
2	$\text{C}_4\text{H}_9\text{S}-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CH}(\text{OC}_2\text{H}_5)_2$ (XII)	2210(3)	1562(3)	1020(6); 1060(10); 1087(8); 1140(8); 1280(3); 1331(4); 1357(4); 1456 (4b)
3	$\text{C}_2\text{H}_5\text{S}-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CH}_2(\text{OC}_2\text{H}_5)-$ $-\text{CH}_2-\text{CH}(\text{OC}_2\text{H}_5)-\text{CH}_2-\text{CH}(\text{OC}_2\text{H}_5)-$ $n=2$ (VIb)	2205(2)	1562(3)	1069(10); 1100(10); 1123(9); 1270(4); 1348(5); 1379(6); 1450(5)
4	$\text{C}_4\text{H}_9\text{O}-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CH}(\text{OC}_2\text{H}_5)_2$ III	2217(4)	1634(7)	1018(6); 1060(10); 1085(9); 1120(8); 1170(8); 1279(5); 1332(6); 1360(6); 1375(6); 1460(4b)
5	$\text{C}_4\text{H}_9\text{O}-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CH}(\text{OC}_2\text{H}_5)-\text{CH}_2-$ $-\text{CH}(\text{OC}_2\text{H}_5)-$ (Va)	2215(3)	1633(6)	1015(5); 1069(10); 1168(7); 1274(5); 1379(6); 1460 (4b)
6	$\text{C}_4\text{H}_9\text{O}-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CH}(\text{OC}_2\text{H}_5)-$ $-\text{CH}_2-\text{CH}(\text{OC}_2\text{H}_5)-\text{CH}_2-\text{CH}(\text{OC}_2\text{H}_5)-$ $n=4$ (Vb)	2213(3)	1635(5)	1070(9); 1100(10); 1165(6); 1247(5); 1380(6); 1450(4)
7	ROC=CR'		$\sim 1660$	
8	RC $\equiv$ CR'	$\sim 2250$		

Table 1 shows that in these compounds hetero atoms affect the frequency of the C=C double bond: in the sulfide acetals (IV) and (XII) and in the products of the addition of vinyl ethers (VIb) it is lower than in 1-buten-3-yne, but in (III), (Va), and (Vb) it is higher. The frequency of the triple C $\equiv$ C bond is high in comparison with the ethynyl vinyl ethers and sulfides investigated by us previously [13], the difference being  $120 \text{ cm}^{-1}$  on the average; this is to be explained by the lengthening of the chain on the triple bond side. It is interesting to note that in the infrared spectra of (III), (Va), and (Vb), as also of vinyl ethers, the double C=C bond band has a complex structure, which is probably associated with rotational isomers [14].

#### EXPERIMENTAL

Reaction of Ethyl Vinyl Ether with 5-Butoxy-4-penten-2-ynal Diethyl Acetal (III). A sealed tube containing 4.0 g (0.017 mole) of the ether acetal (III), 3.6 g (0.051 mole) of ethyl vinyl ether, and 1 ml of a saturated solution of  $\text{ZnCl}_2$  in ether was heated in a metal bath at  $100-110^\circ$  for six hours. When cool, the reaction mixture was diluted with ether, washed with water, and dried over sodium sulfate; unchanged ethyl vinyl ether was distilled off, and the residue was vacuum-distilled (Expt. 1, Table 2).



TABLE 2

Proportions of reactants		Yield of fractions (%)		
		I, 75-85° (0.003 mm)	II, 87-102° (0.003 mm)	III, 103- 130° (0.003 mm)
Ether acetal	Ethyl vinyl ether			
1	3	17.5	18.1	66.6
1	2	23.2	23.5	64.7
1	1	46.0	62.9	4.8

From Fraction III distillation gave the  $C_{15}$  product of the addition of five molecules of ethyl vinyl ether (Vb); b.p. 126° (0.005 mm);  $n_D^{20}$  1.4520;  $d_4^{20}$  0.9921. Found: C 67.54; 67.27; H 10.30; 10.46%.  $C_{33}H_{62}O_8$ . Calculated: C 67.54; H 10.65%.

The results of experiments carried out with various proportions of reactants are given in Table 2.

Reaction of Ethyl Vinyl Ether with 5-(Ethylthio)-4-penten-2-ynal Diethyl Acetal (IV). A sealed tube containing 3 g (0.0014 mole) of the sulfide acetal (IV), 3 g (0.041 mole) of ethyl vinyl ether, and 0.4 ml of a saturated solution of  $ZnCl_2$  in ether was heated in a metal bath at 115-120° for six hours. The mixture was washed with water, dried over sodium sulfate, and, after removal of unchanged ethyl vinyl ether, vacuum-fractionated.

TABLE 3

Proportions of reactants		Yield of fractions (%)		
		I, 73-85° (0.007 mm)	II, 86-110° (0.007 mm)	III, 115- 135° (0.007 mm)
Sulfide acetal	Ethyl vinyl ether			
1	3	30.0	19	76
1	2	54.3	23	57
1	1	57.6	72	13

Fraction I (0.7 g) consisted of unchanged ether acetal (III);  $n_D^{20}$  1.4690; b.p. 77° ( $9 \cdot 10^{-4}$  mm) [2]. Fractions II and III (0.6 and 2.2 g), collected from several experiments, were fractionated. From Fraction II fractionation gave 7-butoxy-1,1,3-triethoxy-4-hexen-3-yne (Va); b.p. 109-110° (0.009 mm);  $n_D^{20}$  1.4600;  $d_4^{20}$  0.9557; found, MR 85.52;  $C_{17}H_{30}O_4$ . Calculated, MR 84.74. Found C 67.81; 68.05; H 9.84; 9.98%; mol. wt. 286.9; 294.2.  $C_{17}H_{30}O_4$ . Calculated: C 68.42; H 10.13%; mol. wt. 298.4.

Fraction I (0.9 g) was unchanged sulfide acetal;  $n_D^{20}$  1.5120; b.p. 85-87° (0.007 mm) [2], and Fractions II and III (0.4 and 1.6 g), collected from several experiments, were fractionated. Fractionation of Fraction II gave 1,1,3-triethoxy-7-(ethylthio)-1-hexen-3-yne (VIa); b.p. 112-113° (0.006 mm);  $n_D^{20}$  1.4932;  $d_4^{20}$  0.9921. Found MR 83.60.  $C_{15}H_{26}SO_3$ . Calculated MR 81.84. Found: C 63.08; 62.94; H 9.48; 9.38; S 10.91; 10.93%; mol. wt. 283.0; 305.2.  $C_{15}H_{26}SO_3$ . Calculated: C 62.90; H 9.15; S 11.17%; mol. wt. 286.4.

Fractionation of Fraction III gave the  $C_{11}$  product of the addition of ethyl vinyl ether molecules (VIb); b.p. 126° (0.003 mm);  $n_D^{20}$  1.4890;  $d_4^{20}$  1.0013; found MR 121.3.  $C_{23}H_{42}SO_5$ . Calculated MR 122.0. Found: C 64.28; 64.30; H 9.96; 9.73; S 7.37; 7.38%. mol. wt. 427.0; 422.7.  $C_{22}H_{42}SO_5$ . Calculated: C 64.14; H 9.83; S 7.44%; mol. wt. 430.65.

The results of experiments\* carried out with various proportions of reactants are given in Table 3.

Reaction of Ethyl Vinyl Sulfide with 5-(Ethylthio)-4-penten-2-ynal Diethyl Acetal (IV). A sealed tube containing 5 g (0.023 mole) of the sulfide acetal (IV), 6 g (0.068 mole) of ethyl vinyl sulfide, 1 ml of a saturated solution of  $ZnCl_2$  in ether, and 5 ml of dioxane was heated at 95-98° for eight hours. The contents of the tube were diluted with ether, and the solution was washed with water and dried over sodium sulfate; after the removal of solvent and ethyl vinyl sulfide it was vacuum-fractionated.

Fraction I (4.2 g) consisted of unchanged sulfide acetal (IV). After repeated chromatography on alumina, Fraction II (0.6 g) from two experiments gave the following products: 1) The  $C_7$  product of the addition of one molecule of ethyl vinyl sulfide (VII);  $n_D^{20}$  1.5312. Found: C 59.78; 59.97; H 8.38; 8.45; S 21.25; 21.39%; mol. wt. 297.6; 304.8.  $C_{15}H_{26}S_2O_2$ . Calculated: C 59.57; H 8.66; S 21.20%; mol. wt. 302.50.

By titration of a weighed sample of the substance with an alcoholic solution of  $HgCl_2$  we found the content of (VII) to be 99.8%.

2) The  $C_9$  product of the addition of two molecules of ethyl vinyl sulfide (IXa);  $n_D^{20}$  1.5828. Found: C 57.96; 57.75; H 8.67; 8.55; S 24.26; 24.28%,  $C_{19}H_{34}S_3O_2$ . Calculated: C 58.42; H 8.77; S 24.62%.

\* For the titration of 0.1482 g of the substance 3.75 ml of 0.7 N NaOH was required, which corresponds to a content of (VIb) of 100.1%.



By titration of a weighed sample of the substance with an alcoholic solution of  $\text{HgCl}_2$  we found the content of (IX) to be 99.3%.

Fraction III as a solution of 1.0 g in 30 ml of petroleum ether was subjected to chromatography on 12.5 g of alumina and was separated into three parts, each 10 ml: Fraction I (0.12 g),  $n_D^{20}$  1.5470; Fraction II (0.39 g),  $n_D^{20}$  1.5440; Fraction III (0.26 g),  $n_D^{20}$  1.5375; residue 0.21 g (eluted with methanol).

Each of the new fractions, collected from several experiments, was subjected to further chromatography under the same conditions, after which we isolated the following substances:

1) The  $\text{C}_7$  product of the addition of one molecule of ethyl vinyl sulfide (VIII);  $n_D^{20}$  1.5440;  $d_4^{20}$  1.0368; found MR 97.99.  $\text{C}_{15}\text{H}_{26}\text{S}_3\text{O}$   $\text{E} \equiv \text{E}$ . Calculated MR 94.99. Found: C 56.58; 56.66; H 8.37; 8.29; S 30.41; 30.29%.  $\text{C}_{15}\text{H}_{26}\text{S}_3\text{O}$ . Calculated: C 56.55; H 8.22; S 30.19%.

By titration of a sample of (VIII) with an alcoholic solution of  $\text{HgCl}_2$  we found the content of (VIII) to be 100.1%.

2) The  $\text{C}_9$  product of the addition of two molecules of ethyl vinyl sulfide (XI);  $n_D^{20}$  1.5414,  $d_4^{20}$  1.0473. Found MR 122.1.  $\text{C}_{19}\text{H}_{34}\text{S}_4\text{O}$   $\text{E} \equiv \text{E}$ . Calculated MR 120.9. Found: C 55.27; 55.40; H 8.02; 8.14; S 31.26; 31.01%.  $\text{C}_{19}\text{H}_{34}\text{S}_4\text{O}$ . Calculated: C 56.10; H 8.42; S 31.52%.

3) The  $\text{C}_{11}$  product of the addition of three molecules of ethyl vinyl sulfide (X);  $n_D^{20}$  1.5373;  $d_4^{20}$  1.0583. Found MR 141.4.  $\text{C}_{23}\text{H}_{42}\text{S}_4\text{O}_2$   $\text{E} \equiv \text{E}$ . Calculated MR 141.04. Found: S 27.11; 27.25%.  $\text{C}_{23}\text{H}_{42}\text{S}_4\text{O}_2$ . Calculated: S 26.78%.

#### SUMMARY

1. For the first time a study has been made of the reaction of vinyl ethers and sulfides with 5-alkoxy- and 5-(alkylthio)-4-penten-2-ynal acetals prepared from butadiyne. The reactions investigated are telomerization reactions and may be applied in effecting growth of the carbon chains of the molecules of unsaturated acetals.

2. The conditions have been found for the participation of vinyl sulfides in ionic telomerization, which makes it possible to introduce sulfur into the molecules of unsaturated acetals.

3. The isolation has been effected of previously undescribed alkoxy and alkylthio acetals containing the enyne grouping and having a carbon chain of 7-15 atoms, and also of  $\text{C}_7$ - $\text{C}_{11}$  alkoxy mercaptals containing up to four alkylthio groups in the molecule; for the separation of these chromatography on alumina was employed.

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# ALKYLATION OF PHENOLS WITH COMPOUNDS WITH MIXED FUNCTIONS

## COMMUNICATION 3. ALKENYLATION OF m- AND p-CRESOLS WITH 3-BUTEN-1-OL

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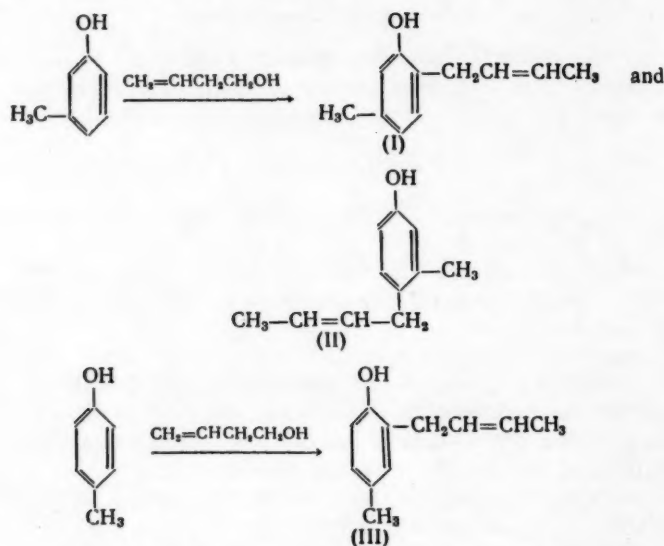
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No. 10, pp. 1847-1851, October, 1961

Original article submitted March 29, 1961

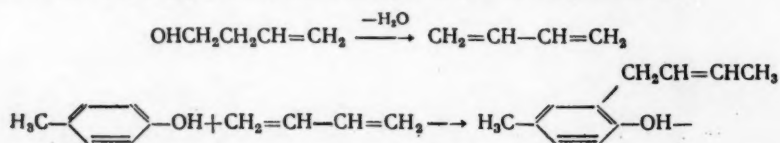
In our first two communications [1,2] we gave the results of the alkenylation of the isomeric cresols with allyl alcohol in presence of acidic catalysts. In this connection it was considered to be of interest to study the alkenylation of isomeric cresols with 3-buten-1-ol, in which the hydroxy group is less affected by the double bond than in the allyl alcohol molecules and approximates in its properties to the hydroxyl of primary alcohols.

For the alkenylation of m- and p-cresols with 3-buten-1-ol it was found to be necessary to raise the temperature somewhat. Thus, in the alkenylation of m-cresol in presence of phosphoric acid the temperature was raised from 70° to 130°. The alkenylation of m- and p-cresols with 3-buten-1-ol was investigated in presence of phosphoric acid and Kationit KU-1. In all the experiments on the alkenylation of m-cresol in presence of phosphoric acid and KU-1 we isolated alkenylphenols in the form of the o- (I) and p-isomers (II); in the alkenylation of p-cresol we obtained only the o-isomer (III):

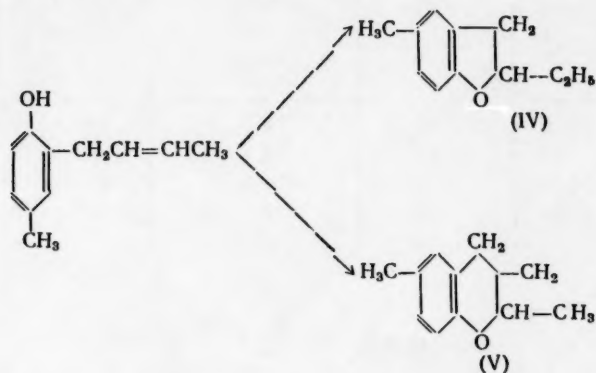


The neutral reaction products consisted of a mixture of the corresponding chroman and coumaran.

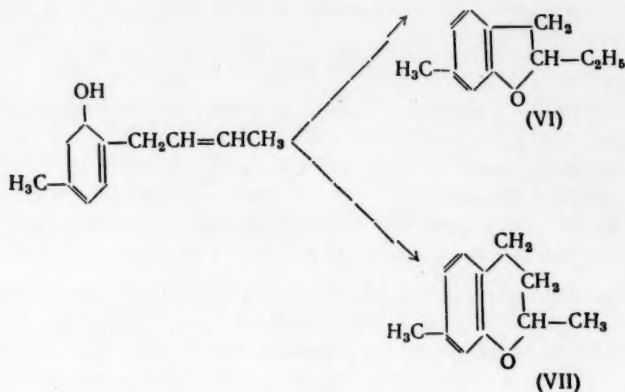
In special experiments we showed that under the given conditions 3-buten-1-ol is converted into butadiene, to which the cresol then adds in the 1,4-positions, as shown by Arbuzov and Shapshinska [3].



This reaction mechanism is supported by the fact that in none of the experiments on the alkenylation of cresols with 3-buten-1-ol was the corresponding butenyl ether isolated. *m*-Cresol butenyl ether, which we synthesized, differed substantially in its properties from the neutral reaction products isolated from the catalyzates. The results of spectrum analysis confirmed the presence of a double bond in the 2,3-position in the side chain in 4-(butenyl)-*m*-cresol. Also, the hydrogenation product of 6-(butenyl)-*m*-cresol and its phenoxy derivative did not differ in properties from 6-butyl-*m*-cresol, prepared by the Clemmensen reduction of 6-butyryl-*m*-cresol, and its phenoxy derivatives. Hence, the butenyl group has a straight carbon chain, which is possible only on addition of the cresol molecule to butadiene in the 1,4-positions. The formation of butenylcresols of the structures indicated is confirmed by the isolation of two neutral cyclization products from the products of the alkenylation of *p*-cresol, namely 2-ethyl-5-methylcoumaran (IV) and 2,6-dimethylchroman (V),



and the isolation from the alkenylation products of *m*-cresol of 2-ethyl-6-methylcoumaran (VI) and 2,7-dimethylchroman (VII)



With the other structure for the butenylcresols there would be formed only 2,3,5-trimethylcoumaran (VIII) in the alkenylation of *p*-cresol and 2,3,6-trimethylcoumaran (IX) in the case of *m*-cresol

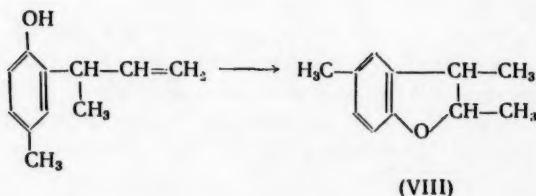
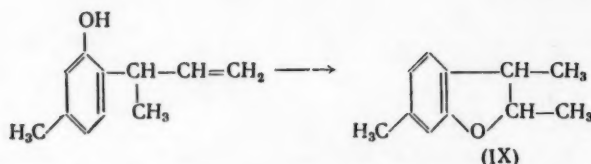


TABLE 1. Results of the Alkenylation of m-Cresol with 3-Buten-1-ol (Molar Ratio 1 : 1)

Catalyst	Amt. of catalyst (% on original reactants)	Temp. (°C)	Time of alkenylation (hr)	Yield of catalyzate (% on original re- actants)	Alkenyla- tion pro- ducts, to- tal yield		Yields of alkenylation products (% on m-cresol that reacted)				
					%	% on m-cresol that reacted	1-Ethyl-6- methylcoumaran	2,7-Dimethyl- chroman	6-(2-Butenyl)- m-cresol	4-(2-Butenyl)- m-cresol	High boiling products and polymers
H <sub>3</sub> PO <sub>4</sub>	200	95-100	16	76.2	30.3	65.7	10.2	9.2	3.6	11	30.7
H <sub>3</sub> PO <sub>4</sub>	200	110	10	80.4	60.4	64.6	20	6.6	6.6	18.6	13.2
H <sub>3</sub> PO <sub>4</sub>	200	125	10	78.3	71.4	73.3	21.4	7.3	traces	20.1	23.9
KU-1	10	120	12	77.2	39.9	63.1	21.5	17.6	1.5	-	22.5



The literature gives only the properties of 2,6-dimethylchroman [4]; they are close to those found in the present work.

#### EXPERIMENTAL

For the investigation we took pure m- and p-cresols. 3-Buten-1-ol was synthesized by Pariselle's method [5]; it has the following properties: b.p. 113-115° (755 mm);  $n_D^{20}$  1.4220;  $d_4^{20}$  0.8352; yield only 24%. According to Pariselle 3-buten-1-ol has the following properties: b.p. 112.5-113.5°;  $n_D^{20}$  1.4224;  $d_4^{20}$  0.8379 [5]. The apparatus and the experimental procedure in the alkenylation of the cresols and the treatment of the catalyzates were described in the first communication [1]. The results of experiments on the alkenylation of m- and p-cresols in presence of the catalysts indicated are presented in Tables 1 and 2 respectively. Table 3 gives the properties of the substances isolated.

We prepared the methyl ethers of phenols (I) and (II) (Table 3), and they had the following properties. Methyl ether of (I): b.p. 87-89° (6 mm);  $n_D^{20}$  1.5234;  $d_4^{20}$  0.9647; found MR 55.84; methyl ether of (II): b.p. 96-98° (6 mm);  $n_D^{20}$  1.5240;  $d_4^{20}$  0.9646; found MR 55.85.  $C_{12}H_{16}O$ . Calculated MR 55.22. By oxidation of the methyl ethers with concentrated permanganate solution, from the ether of phenol (I) we obtained an acid of m.p. 273-274°, which corresponds to methoxyterephthalic acid (m.p. 275°) [6], and from the methyl ether of phenol (II) we obtained an acid of m.p. 162-164°, which corresponds to 4-methoxyphthalic acid [6]. For the identification of the phenols isolated we prepared also their phenoxyacetic acids. The melting point of the phenoxyacetic acid from phenol (II) was 109-109.5°. Found: C 70.74; H 7.31%.  $C_{13}H_{16}O_3$ . Calculated: C 70.91; H 7.18%. The melting point of the phenoxyacetic acid from phenol (I) was 106-108°.

The hydrogenation of phenols (I) and (II) was carried out in alcoholic solution in presence of Raney nickel at 40°. From 4 g of 6-(2-butenyl)-m-cresol we obtained 3.4 g of 6-butyl-m-cresol; b.p. 108-110° (5 mm); m.p. 17-18°;  $n_D^{20}$  1.5192;  $d_4^{20}$  0.9654. The melting point of the phenoxy derivative was 84-85°, undepressed in admixture with the phenoxy derivative of 6-butyl-m-cresol obtained by the Clemmensen reduction of 6-butyl-m-cresol. For 6-butyl-m-cresol the literature [7] gives: b.p. 132-134° (15 mm); m.p. 18°. From the phenol (II) under similar conditions we obtained 4-butyl-m-cresol: b.p. 116-118° (5 mm); m.p. 24-25°. The phenoxy derivative had m.p. 93-94°. Found: C 69.97; H 8.14%.  $C_{13}H_{18}O_3$ . Calculated: C 70.15; H 8.15%.

TABLE 2. Results of the Alkenylation of p-Cresol with 3-Buten-1-ol

Molar ratio of cresol to 3-buten-1-ol	Catalyst	Amt. catalyst (% on original reactants)	Temp. (°C)	Time of alkenylation (hr)	Yield of catalyst (% on original reactants)	Alkenylation products, total yield		Yields of alkenylation products (% on p-cresol that reacted)			
						% on original 3-buten-1-ol	% on p-cresol that reacted	2-ethyl-5-methylcoumaran	2,6-dimethylchroman	2-(2-butenyl)-p-cresol	high-boiling products and polymers
1 : 1	H <sub>3</sub> PO <sub>4</sub>	200	125	10	80.7	80.0	90.7	26.6	23.3	—	40.8
2 : 1	H <sub>3</sub> PO <sub>4</sub>	200	135-140	10	80.3	89.2	99.2	25.2	26.9	1.5	45.6
2 : 1	KU-1	10	120	10	74.8	70.0	62.2	12.6	13.5	—	43.1

TABLE 3. Properties of Substances Isolated as a Result of the Alkenylation of m- and p-Cresols with 3-Buten-1-ol

No.	Substance	B.p. in °C (p in mm)	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	MR	
					found	calculated
I	6-(2-Butenyl)-m-cresol	101-103(3)	1.5391	1.0062	50.46	50.45
II	4-(2-Butenyl)-m-cresol	108-110(3)	1.5402	1.0053	50.58	50.45
III	2-(2-Butenyl)-p-cresol	106-110(7)	1.5330	0.9994	50.30	50.45
IV	2-Ethyl-6-methylcoumaran	110-111(14)	1.5250	0.9910	50.07	48.86
V	2-Ethyl-5-methylcoumaran	93-95(6)	1.5238	0.9948	49.75	48.86
VI	2,7-Dimethylchroman	118-120(14)	1.5290	0.9980	50.07	48.86
VII	2,6-Dimethylchroman	99-101(6)	1.5268	0.9978	49.90	48.86

**Transformations of 3-Buten-1-ol under the Experimental Conditions.** A mixture of 12 g of 3-buten-1-ol and 29 ml of phosphoric acid was prepared in a round-bottomed flask fitted with reflux condenser and tube for the removal of the gases formed. The mixture was heated to 125°, and the gas liberated was absorbed in bromine water, which was then treated with ether. The ether extract was dried, ether was distilled off, and the crystals of bromo derivative that remained were recrystallized from alcohol; they had m.p. 38-39°, which is close to the melting point of tetrabromobutane (40°). The nonphenolic part of the catalysts was distilled through a vacuum column of 20-plate efficiency. We isolated the substances (IV), (V), (VI), and (VII), the properties of which are given in Table 3. To confirm the structures of the neutral substances (IV) and (V) isolated they were heated with N,N-dimethylaniline in an oil bath for three hours. After removal of dimethylaniline by washing with concentrated sulfuric acid, the residue was treated with concentrated sodium hydroxide solution. No butenylcresols could be isolated from the alkaline extract. Hence, the substances (IV) and (V) do not undergo the Claisen rearrangement and are not butenyl ethers of isomeric cresols. To confirm this we synthesized butenyl m-tolyl ether by heating sodium tolyl oxide with 4-chloro-1-butene. Butenyl m-tolyl ether had b.p. 83-86° (4-5 mm); n<sub>D</sub><sup>20</sup> 1.5194; d<sub>4</sub><sup>20</sup> 0.9738.

## SUMMARY

1. An investigation was made of the alkenylation of m- and p-cresols with 3-buten-1-ol in presence of phosphoric acid and Kationit KU-1.
2. As a result of the alkenylation the corresponding butenylcresols and their cyclization products (chromans and coumarans) were formed.
3. The alkenylation of cresols with 3-buten-1-ol proceeds by a mechanism that differs from that of their alkenylation by allyl alcohol in presence of the same catalysts.

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# ALKYLATION OF PHENOLS WITH COMPOUNDS WITH MIXED FUNCTIONS

## COMMUNICATION 4. ALKENYLATION OF m- AND p-CRESOLS WITH 4-PENTEN-1-OL

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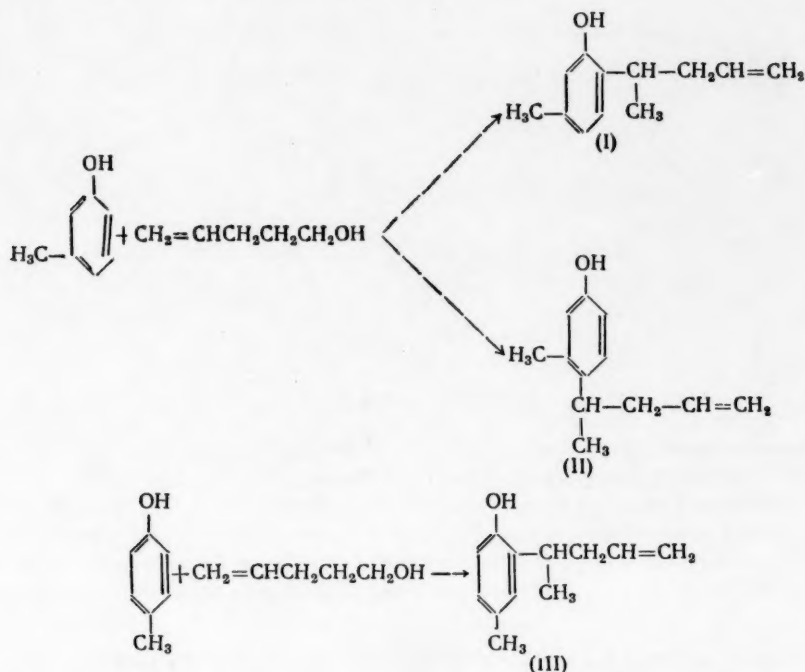
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 10, pp. 1851-1855, October, 1961

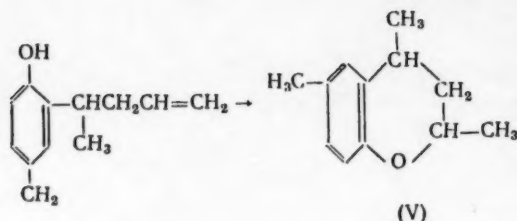
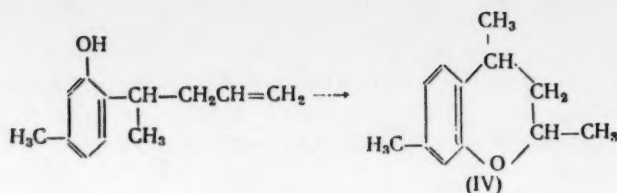
Original article received March 29, 1961

Continuing the study of alkenylation with unsaturated alcohols [1-3], we studied the alkenylation of isomeric cresols with 4-penten-1-ol in presence of phosphoric acid. It was found that this reaction requires a higher temperature (135-140°). Under such conditions the reaction proceeds almost quantitatively, but a considerable amount of high-boiling and polymeric substances and of neutral reaction products is formed.

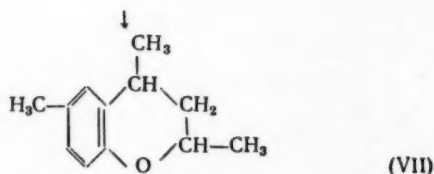
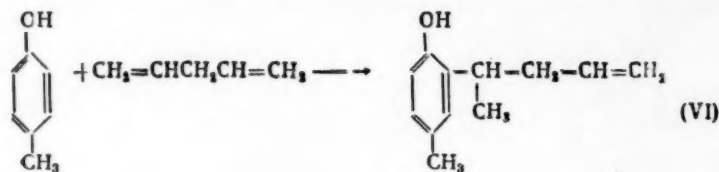
In all experiments on the alkenylation of m-cresol we isolated the alkenylphenol as the o- (I) and p-isomers (II); in the alkenylation of p-cresol we obtained only the o-isomer (III).



These structures for our products are supported by the results of the hydrogenation of the phenols (I) and (II). In the catalytic hydrogenation of these phenols we obtained 6- and 4-s-pentyl-m-cresols, for which the properties and the melting points of the phenoxy derivatives coincide with those for 6- and 4-s-pentyl-m-cresols prepared in our laboratory by the hydrogenation of the products of the alkylation of m-cresol with piperylene [4]. Confirmation of such structures of the alkenylphenols isolated is provided by the structures of the neutral reaction products, 2, 4, 7- (IV) and 2, 4, 6-trimethylchromans (V),



whose constants coincide with those of 2, 4, 7- and 2, 4, 6-trimethylchromans prepared in our laboratory by the alkenylation of *m*- and *p*-cresols with piperylene [4, 5]. Hence, alkenylation with 4-penten-1-ol proceeds under more severe conditions and by a different mechanism than in the case of allyl alcohol. 1, 4-Pentadiene is probably an intermediate product, and this reacts further with cresol:



## EXPERIMENTAL

For the investigation we took pure *m*- and *p*-cresols. We synthesized 4-penten-1-ol by Kirner's method [6] by the action of sodium on tetrahydrofurfuryl chloride; it had the following properties: b.p. 135-137° (750 mm);  $n_D^{20}$  1.4364;  $d_4^{20}$  0.8487. According to Kirner 4-penten-1-ol has the following properties: b.p. 138-142° (760 mm);  $n_D^{20}$  1.4365;  $d_4^{20}$  0.8492 [6]. The yield of 4-penten-1-ol was 86%. The apparatus and the experimental procedure in the alkenylation of the cresols and the treatment of the catalyzates are described in [1]. The results of experiments on the alkenylation of *m*- and *p*-cresols are presented in Tables 1 and 2 respectively. Table 3 gives the properties of the substances isolated from the catalyzates.

Solaway and Santoro's qualitative reaction [7] indicated a free *p*-position in the phenol (I) (Table 3). For the phenol (II) we prepared the methyl ether, which had the following properties: b.p. 106-108° (8 mm);  $n_D^{20}$  1.5214;  $d_4^{20}$  0.9582; found MR 59.82.  $\text{C}_{13}\text{H}_{18}\text{O}_2$ . Calculated MR 59.80. By oxidation of the methyl ether with concentrated permanganate solution we obtained an acid of m.p. 162-164°, which is close to the melting point of 4-methoxyphthalic acid (166°) [8]. As the yield of the phenol (III) was extremely low, for its identification we prepared only the phenox-yacetic acid, m.p. 118-120.5°.

The hydrogenation of the phenols (I) and (II) was carried out in alcoholic solution in presence of Raney nickel at 40°. From 4 g of the phenol (I) we obtained 3.6 g of 6-*s*-pentyl-*m*-cresol with the following properties: b.p. 102-104° (3-4 mm);  $n_D^{20}$  1.5188;  $d_4^{20}$  0.9627; found MR 56.03.  $\text{C}_{12}\text{H}_{18}\text{O}$ . Calculated MR 55.54. The melting point of the phenoxy derivative was 97-98°.

TABLE 1. Results of the Alkenylation of m-Cresol with 4-Penten-1-ol (Molar Ratio 1:1) in Presence of Phosphoric Acid

Expt.	Amt. of catalyst (% on reactants)	Temp. (°C)	Time of alkylation (hr)	Yield of catalyzate (% on reactants)	Total yield of alkeny- lation products		Yields of alkenylation products (% on m-cresol that reacted)			
					% of theo- retical	% on m cresol that re- acted	2, 4, 7-Tri- methyl- chroman	6-(1-Methyl- 3-butenyl)- m-cresol	4-(1-Methyl- 3-butenyl)- m-cresol	High-boiling products and polymers
1	200	100	8	75.5	20.6	38.5	13.1	4.7	16.7	43
2	200	120	8	87.1	58.4	85.5	33.1	6.9	31.5	13.8
3	200	135	8	88.2	89.8	97.3	39.3	—	37.5	20.5
4	200	150	8	86.4	86.5	91.8	32.3	—	33.7	25.8

TABLE 2. Results of the Alkenylation of p-Cresol with 4-Penten-1-ol (Molar Ratio 1 : 1) in Presence of Phosphoric Acid

Expt.	Amt. of catalyst (% on re-actants)	Temp. (°C)	Time of alkylation (hr)	Yield of catalyzate (% on re-actants)	Total yield of alkenylation products		Yields of alkenylation products (% on p-cresol that reacted)		
					% of theoretical	% on p-cresol that reacted	2, 4, 6-Tri-methylchroman	2-(1-Methyl-3-butenyl)-p-cresol	High-boiling products and polymers
1	200	135-140	10	75.4	51.6	98.8	40.9	4.8	52.4
2	200	150-155	10	85.2	77.7	93.3	35.2	1.1	55.3

TABLE 3.

No.	Substance	B. p. in °C (p in mm)	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	MR	
					found	calculated
I	6-(1-Methyl-3-butenyl)-m-cresol	131-133(8-9)	1.5322	0.9872	55.24	55.07
II	4-(1-Methyl-3-butenyl)-m-cresol	139-141(8-9)	1.5372	0.9882	55.53	55.07
III	2-(1-Methyl-3-butenyl)-p-cresol	120-122(6)	1.5327	1.0096	54.11	55.07
IV	2, 4, 7-Trimethylchroman	112-112.5(9)	1.5199	0.9845	54.46	53.46
V	2, 4, 6-Trimethylchroman	104-106(6)	1.5210	0.9858	54.2	53.46

From 6 g of the phenol (II) we obtained 4.9 g of 4-s-pentyl-m-cresol with the following properties: b.p. 112-114° (4 mm); n<sub>D</sub><sup>20</sup> 1.5194; d<sub>4</sub><sup>20</sup> 0.9678; found MR 55.84, C<sub>12</sub>H<sub>18</sub>O = 3. Calculated: MR 55.54. The melting point of the phenoxycetic acid was 111-112.5°. Data in the literature [7]: 6-s-pentyl-m-cresol-b.p. 103-104° (3 mm); n<sub>D</sub><sup>20</sup> 1.5190; d<sub>4</sub><sup>20</sup> 0.9621; 4-s-pentyl-m-cresol-b.p. 110-112° (3 mm); n<sub>D</sub><sup>20</sup> 1.5194; d<sub>4</sub><sup>20</sup> 0.9678.

The nonphenolic part of the catalyzate was fractionated through a vacuum column of 20-plate efficiency. We isolated the substances (IV) and (V), the properties of which are given in Table 3. To ensure that the products isolated were not pentenyl tolyl ethers we carried out the Claisen rearrangement with N, N-dimethylaniline. We isolated only unchanged (IV) and (V). The substances that we obtained were close in properties to 2, 4, 6- and 2, 4, 7-trimethylchromans, prepared in our laboratory by the alkenylation of m- and p-cresols with piperylene [4, 5]. The literature gives: 2, 4, 6-trimethylchroman; b.p. 91-93° (3 mm); n<sub>D</sub><sup>20</sup> 1.5219; d<sub>4</sub><sup>20</sup> 0.9857; [5]: 2, 4, 7-Trimethylchroman; b.p. 114.5-116° (10 mm); n<sub>D</sub><sup>20</sup> 1.5200; d<sub>4</sub><sup>20</sup> 0.9822 [5].

#### SUMMARY

1. An investigation was made of the alkenylation of m- and p-cresols with 4-penten-1-ol in presence of phosphoric acid.

2. As a result of the alkenylation the corresponding (methylbutenyl) cresols and their cyclization products (chromanes) were obtained.

3. The alkenylation of cresols with 4-penten-1-ol proceeds by a mechanism that differs from that of alkenylation with allyl alcohol. 1, 4-Pentadiene forms an intermediate product in the reaction.

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## CATALYTIC SYNTHESIS OF NITRILES

## COMMUNICATION 5. CONVERSION OF ISOALKANOLS INTO NITRILES

### BY MEANS OF AMMONIA

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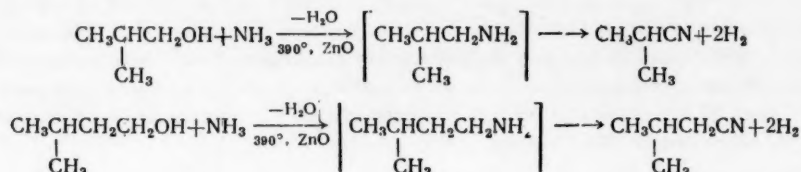
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The regularities observed [1] by us in the preparation of nitriles by the catalytic treatment of normal saturated aliphatic alcohols with ammonia prompted us to continue this investigation. The object of the present work was to determine the effect of branching of the carbon chain of the alcohol on the nitrile-formation reaction. For this purpose the following primary alcohols were used: isobutyl and isopentyl alcohols. Experiment showed that in this case a nickel-alumina catalyst is unsuitable because of considerable decomposition of the alcohols in its presence. With a view to the avoidance of this trouble we investigated oxide catalysts having a dehydrating and a dehydrogenating action, and we determined the optimum conditions for their use. Among these catalysts the most effective was found to be zinc oxide, in the presence of which nitrile formation from the primary alcohols taken for investigation proceeded smoothly, probably passing through the intermediate stage of primary-amine formation.



## EXPERIMENTAL

The alcohols taken for investigation had the following properties: Isobutyl alcohol had b.p. 107-108° (758 mm);  $d_4^{20}$  0.8047;  $n_D^{20}$  1.3960. According to the literature: b.p. 107.53° [2];  $d_4^{16.35}$  0.80459 [3];  $n_D^{20}$  1.3966 [4]. Isopentyl alcohol had: b.p. 132-132.5°;  $d_4^{20}$  0.8042;  $n_D^{20}$  1.4055. The literature [5] gives: b.p. 132-132.1°;  $d_4^{20}$  0.8044;  $n_D^{25}$  1.4046.

The nitrile formation was carried out in the apparatus described in the first communication [1]. The methods of estimating the nitrile and separating the components of the catalyzate are given in the same place. In all experiments the molar ratio of ammonia to alcohol was about two; the space velocity of the feed of the alcohol to the catalyst was  $0.2 \text{ hr}^{-1}$ ; the volume of catalyst in the tube was 65 ml in a layer of length 45 cm. The duration of the experiment was generally one hour. Five-hour experiments were also carried out to check the stability of the catalyst and to obtain a sufficient amount of catalyzate collected under constant conditions.

The results of nitrile formation from isobutyl alcohol under the action of ammonia are given in Table 1. In each experiment we took 10.4 g of isobutyl alcohol and 4.8 g of ammonia. In the presence of nickel-alumina catalysts at 330-390° we obtained catalyzates containing 86-99% of isobutyronitrile. However, under these conditions the amount of the nonaqueous part of the catalyzate fell with rise in temperature and increase in the nickel content of the catalyst because of the decomposition of the alcohol. Thus, in Expt. 12, carried out at 360° in presence of 15% of nickel on active alumina, from 10.4 g of isobutyl alcohol we obtained only 2.2 g of the nonaqueous part of the catalyzate. We therefore sought for other catalysts effective in the conversion into nitrile. It was found that the addition of 25% or 50% of zinc oxide instead of nickel to the alumina preserves the alcohol from decomposition while not lowering the nitrile content of the catalyzate. In presence of these catalysts at 390° we obtained catalyzates containing 81.8% and 87.2%,

TABLE 1. Catalytic Nitrile Formation from Isobutyl Alcohol

Expt.	Temp.	Catalyst	Amt. of catalyzate obtained		Nitrile content of cata. (%)
			Total	Dry	
1	300	3,5% Ni on Al <sub>2</sub> O <sub>3</sub>	13,6	8,4	70,3
2	330	The same	10,8	6,0	87,4
3	360	» »	8,8	5,2	92,6
4	390	» »	6,6	3,9	95,1
5	420	» »	0,9	—	—
6	300	7,5% Ni on Al <sub>2</sub> O <sub>3</sub>	9,8	7,4	88,4
7	330	The same	9,2	7,0	96,4
8	360	» »	8,2	4,2	99,8
9	390	» »	0,7	—	—
10	300	15% Ni on Al <sub>2</sub> O <sub>3</sub>	9,1	4,0	60,3
11	330	The same	6,5	2,4	86,3
12	360	» »	6,0	2,2	89,4
13	330	25% ZnO on Al <sub>2</sub> O <sub>3</sub>	11,6	8,8	14,7
14	360	The same	10,5	6,6	52,5
15	390	» »	9,6	5,6	81,8
16	420	» »	8,6	2,5	99,4
17	330	50% ZnO on Al <sub>2</sub> O <sub>3</sub>	12,0	8,7	57,4
18	360	The same	12,0	8,5	64,5
19	390	» »	10,0	9,0	87,2
20	420	» »	9,7	6,5	98,7
21	360	100% ZnO	12,3	9,7	67,5
22	390	The same	12,4	9,3	88,9
23	420	» »	12,2	9,2	82,7
24-1	390	» »	12,7	9,9	88,7
24-3	390	» »	12,4	9,1	88,8
24-5	390	» »	12,7	9,5	87,7

respectively, of isobutyronitrile (experiments 15 and 19). Here, from 10.4 g of the alcohol we obtained 5.6 g and 9.0 g, respectively, of the nonaqueous part of the catalyzate. Hence, increase in the zinc oxide content of the catalyst preserves the alcohol from decomposition and only slightly reduces nitrile formation. These facts prompted us to use pure zinc oxide as catalyst for the nitrile formation. Expt. 22 showed that, in presence of pure zinc oxide at the optimum temperature of 390°, from 10.4 g of isobutyl alcohol we obtained 12.4 g of catalyzate, the nonaqueous part of which amounted to 9.3 g and contained 88.9% of nitrile.

With zinc oxide as catalyst a five-hour control experiment was carried out at 390°. Table 1 gives data for the first, third, and fifth hours (Expt. 24). In the course of this experiment 52.0 g of isobutyl alcohol was consumed altogether, and we obtained 49.6 g of dry nonaqueous part of the catalyzate containing 87.9% of nitrile. From 44.0 g of this catalyzate we isolated 0.05 g of amines, 1.1 g of unchanged alcohol, and 32.1 g of nitrile, which had: b.p. 101-102° (748 mm);  $d_4^{20}$  0.7726;  $n_D^{20}$  1.3748; MR 20.45. Part of the nitrile isolated was hydrolyzed to the acid, which melted at 105°. For isobutyronitrile the literature [6] gives b.p. 103-103.5°, and  $d_4^{16.25}$  0.7731; MR calculated is 20.28; isobutyranilide has m.p. 105°.

On the basis of the data cited it may be considered that the substance that we isolated was isobutyronitrile; the yield was 76.6%. In the control experiment (Expt. 24) the gas obtained in one hour amounted to 5880 ml (STP) and contained 99.5% of hydrogen, which indicates the smoothness with which the dehydrogenation of the intermediately formed amines occurred.

Table 2 gives experimental data on nitrile formation from isopentyl alcohol. In order to obtain comparable data, in each experiment we took 10.5 g of isopentyl alcohol and 4.4 g of ammonia. The first three experiments were carried out with 7.5 % nickel-alumina catalyst. Considerable decomposition of the alcohol was noted. In Expt. 3 from 10.5 g of isopentyl alcohol we obtained 10.0 g of catalyzate, the nonaqueous part of which amounted to only 5.3 g. Further experiments were therefore carried out with zinc oxide as catalyst. Decomposition of the alcohol then became appreciable only at 450°. At this temperature from 10.5 g of isopentyl alcohol we obtained 11.4 g of catalyzate containing 8.2 g of nonaqueous part.

When account is taken of the yields of the catalyzates and their nitrile contents it must be considered that 390° is the optimum temperature for nitrile formation from isopentyl alcohol. This is close to the optimum temperature for isobutyl alcohol. At this temperature a five-hour experiment was carried out, and in the course of this 52.5 g of the alcohol was consumed, and we obtained 45.8 g of nonaqueous part of the catalyzate containing 76.3% of nitrile.

TABLE 2. Catalytic Nitrile Formation from Isopentyl Alcohol

Expt.	Temp.	Catalyst	Amt. of catalyzate obtained		Nitrile content of Cata. (%)
			total	dry	
1	300	7,5% Ni on $\text{Al}_2\text{O}_3$	10,4	6,2	89,8
2	330	The same	10,2	5,6	89,9
3	360	" "	10,0	5,3	90,0
4	330	100% ZnO	12,6	10,1	15,1
5	360	The same	11,3	9,6	62,0
6	390	" "	11,7	9,8	77,7
7	420	" "	11,5	9,0	84,7
8	450	" "	11,4	8,2	95,4
9	480	" "	4,8	3,3	99,7
10-1	390	" "	11,4	9,0	76,1
10-3	390	" "	12,2	9,8	76,4
10-5	390	" "	11,8	9,3	76,0

From 42.0 g of this catalyzate we isolated 0.15 g of amines, 5.4 g of unchanged isopentyl alcohol, and 28.7 g of nitrile; b.p. 126-128° (753 mm);  $d_4^{20}$  0.8051;  $n_D^{20}$  1.3921; MR 24.57. The anilide of the acid prepared from the nitrile isolated had m.p. 110°. For isovaleronitrile the literature [6] gives: b.p. 128.5°;  $d_4^{20}$  0.8054; calculated MR 24.90. Isovaleranilide has m.p. 110°. On the basis of the data cited it must be considered that the substance isolated was isovaleronitrile. In expt. 10 the gas obtained in one hour amounted to 4460 ml (STP) and contained 98% of hydrogen and 1% of unsaturated hydrocarbons. When the amount of the alcohol remaining unchanged is taken into account, the yield of isovaleronitrile amounts to 71.4%.

## SUMMARY

An effective catalyst for the conversion of isoalkanols into nitriles under the action of ammonia is pure zinc oxide at 390°. In presence of zinc oxide at this temperature, isobutyl alcohol reacts with ammonia with formation of isobutyronitrile in yields of up to 76.6% and isopentyl alcohol gives isovaleronitrile under the same conditions in yields of up to 71.4%.

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# DETERMINATION OF THE INDIVIDUAL HYDROCARBON COMPOSITION OF TARTARY PETROLEUMS

## COMMUNICATION 6. LIGROIN FROM PETROLEUM FROM THE SHUGUROV DEPOSITS

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In previous communications [1,2] we described ligroins from petroleum of the Romashkin and Bablin districts of Tartary associated with Devonian deposits. It was of interest to study the distribution of hydrocarbons of various classes in petroleum associated with the carbonate deposits of the carboniferous system (C). In the present paper we describe ligroin of b.p. 150-200° of petroleum of the Shugurov deposit (bore hole 10, carboniferous C).

### EXPERIMENTAL

The principal methods used in this investigation are similar to those described in previous papers [1]. The difference lies in the fact that in the present investigation a wide distillate, i.e., from the start of boiling (26°) to 240°, was produced from the petroleum and this was then fractionated through a column of 40-plate efficiency into two fractions: 1) from the start of boiling to 60° (until aromatics made their appearance); 2) b.p. 60-205°. We proposed to investigate also the gasoline part boiling up to 150° (this will be described separately). The separation of the fraction of b.p. 60-205° into two parts was not carried out, and with this fraction we carried out all analytical operations: adsorption separation, catalysis, and the rectifying fractionation of prepared samples.

In the adsorption of the original fraction of b.p. 60-205° ( $d_4^{20}$  0.7566;  $n_D^{20}$  1.4180) we obtained 89.8% of naphthene-paraffin part ( $d_4^{20}$  0.7365;  $n_D^{20}$  1.4115) and 7.5% of aromatic hydrocarbons  $A_1$  ( $d_4^{20}$  0.8744;  $n_D^{20}$  1.4993). On dehydrogenation of the naphthene-paraffin part we isolated a catalyzate in 94.0% yield ( $d_4^{20}$  0.7396;  $n_D^{20}$  1.4150), by the adsorption of which we obtained 85.8% of a mixture of cyclopentane and paraffin hydrocarbons and 9.3% of aromatic hydrocarbons  $A_2$ .

TABLE 1

Fraction	Boiling limits °C	Content in ligroin, %	$d_4^{20}$	$n_D^{20}$	$R_A^*$	$R_N^{**}$
I	150 —162	1,59	0,8623	1,4945	1,00	—
II	163 —167	0,71	0,8734	1,5012	1,01	—
III	167 —174	1,00	0,8760	1,5028	1,02	—
IV	174 —179	0,57	0,8784	1,5018	1,02	0,07
V	179 —182,5	0,76	0,8698	1,4962	0,99	—
VI	182,5—185,5	0,73	0,8728	1,4994	1,01	—
VII	185,5—191	0,92	0,8808	1,5032	1,03	0,09
VIII	191 —195	0,65	0,8850	1,5041	1,03	0,15
IX	195 —200	1,18	0,8853	1,5068	1,05	0,10
	Residue	2,96				
	Losses	0,42				
Total		11,50				

\* $R_A$  is the number of aromatic rings in the aromatic fraction.

\*\* $R_N$  is the number of naphthene rings in the aromatic fraction.

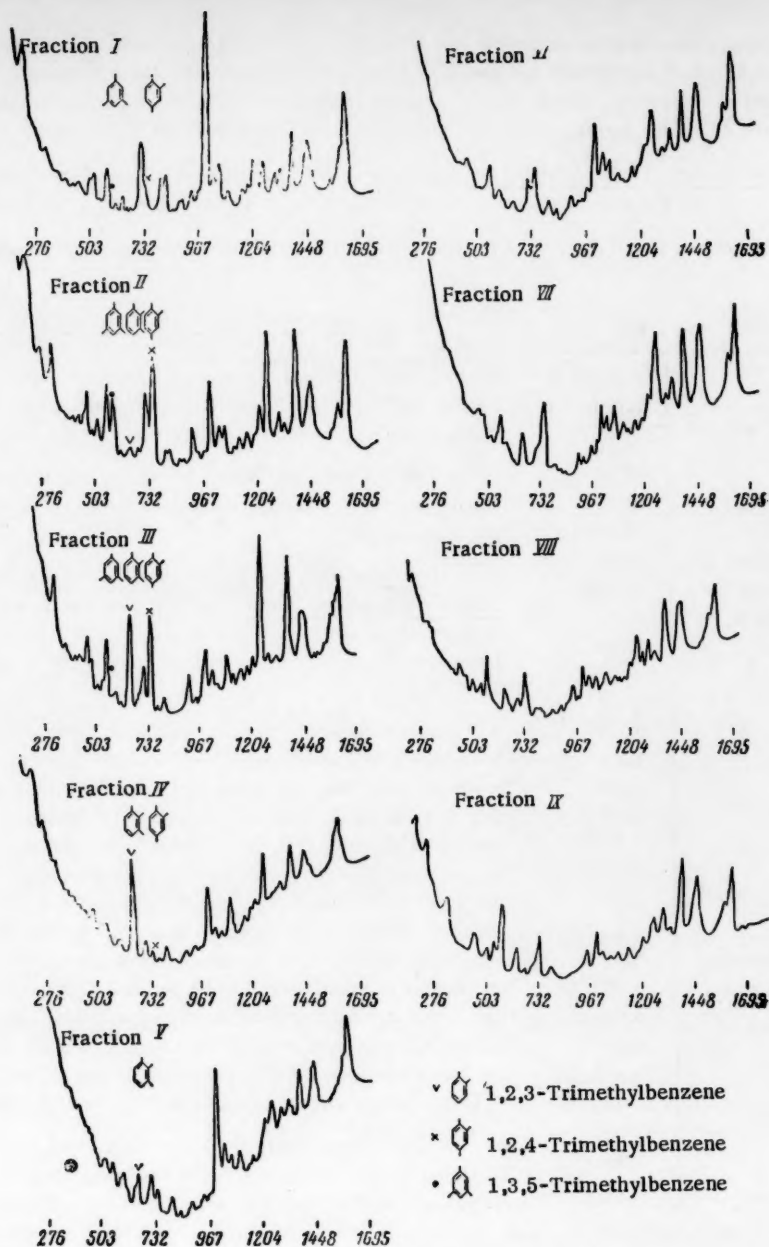


Fig. 1

Narrow fractions of the aromatic hydrocarbons  $A_1$  and  $A_2$  obtained by their fractionation through the 40-plate column were investigated for their contents of aromatic and naphthene rings by the specific-dispersion method [3], and their individual hydrocarbon compositions were investigated by the photographic method with a Soviet ISP-51 three-prism spectrograph with an f-270 camera with a single-lamp illumination. The Raman spectrum was excited by the blue lines of mercury (4358 Å, 4047 Å). The frequencies were measured with an IZA-2 horizontal comparator. As well as the photographic method, we tried the photoelectric method of spectrum registration on an FEP-1 photoelectric attachment. The spectrum of the aromatic hydrocarbons  $A_1$  of the ligroin, determined on the FEP-1, is given in the figure.

The mixture of cyclopentane and paraffin hydrocarbons was also fractionated into narrow fractions, one part of which (up to 150°) was investigated by the spectrum method; for the other part (ligroin) the group composition was



calculated from the specific refractions of narrow fractions [4]. According to the results of adsorption the ligroin consisted of a mixture of 85.3% of naphthenes and paraffins and 11.5% of aromatics. On dehydrogenation of the naphthenes and paraffins the yield of catalyzate was 92.3%; the catalyzate consisted of 81.3% of cyclopentanes and paraffins and 13.1% of aromatics (10.4% on the ligroin, or 10.8% calculated on the converted cyclohexanes).

Composition of Aromatic Hydrocarbons A<sub>1</sub> of Ligroin. On fractionation of 70.3 g of aromatic hydrocarbons A<sub>1</sub> we obtained narrow fractions, the amounts and constants of which are given in Table 1.

The individual composition of the aromatic hydrocarbons, determined by the spectrum method, is given in Table 2.

TABLE 2

Fraction	Content in ligroin (%)
Propylbenzene	0.16
o-Ethyltoluene	0.04
m-Ethyltoluene	0.75
p-Ethyltoluene	0.47
1,2,3-Trimethylbenzene	0.44
1,2,4-Trimethylbenzene	1.14
1,3,5-Trimethylbenzene	0.34
s-Butylbenzene	0.13
Butylbenzene	0.16
m-Cymene	0.03
m-Propyltoluene	0.04
p-Cymene	0.06
p-Propyltoluene	0.04
3-Ethyl-o-xylene	0.17
4-Ethyl-o-xylene	0.32
2-Ethyl-m-xylene	0.04
5-Ethyl-m-xylene	0.25
o-Diethylbenzene	0.17
1,2,3,4-Tetramethylbenzene	0.25
1,2,3,5-Tetramethylbenzene	0.83
o-Diisopropylbenzene	0.03
m-Diisopropylbenzene	0.03
Cumene	Traces
Indan	Traces
2-Ethyl-p-xylene	Traces
Identified	5.89
Not identified	2.25

Composition of the Aromatic Hydrocarbons A<sub>2</sub> of the Ligroin, Obtained in the Catalytic Treatment. By the fractionation of 61 g of the aromatic hydrocarbons isolated from the catalyzate we obtained narrow fractions, the constants and amounts of which are given in Table 3 (calculated on the naphthenes).

Table 4 gives the results of Raman spectrum analysis of the resulting fractions of aromatic hydrocarbons, expressed as the corresponding naphthenes.

Determination of the Structural-Group Composition of the Mixture of Cyclopentanes and Paraffins. On fractionation of 135 g of the mixture of paraffins and cyclopentanes we obtained 13 g of narrow fractions, the group composition and constants of which are given in Table 5.

On the basis of Tables 1-5 and the figure we may make the following generalizations regarding the chemical composition of the ligroin obtained from Shugurov petroleum. It follows from Table 1 that in some of the narrow fractions of the aromatic hydrocarbons A<sub>1</sub> (Fractions IV, VII, VIII, IX) hydrocarbons containing naphthene rings are present. In Fraction IV the presence of a naphthene ring indicates the presence of indan, b.p. 177.9°, among the aromatic hydrocarbons, which is confirmed by spectrum analysis. By this method we did not succeed in determining the structures of the naphthene-aromatic hydrocarbons in Fractions VII, VIII, and IX. The analogous Table 3, which reflects the composition of the aromatic hydrocarbons A<sub>2</sub>, indicates the presence of naphthene rings in almost all fractions, and the considerable amount in Fractions III and IV indicates the presence of indan, which was again confirmed by spectrum analysis.

Table 2 shows that, as in ligroins studied previously, among the C<sub>9</sub> aromatic hydrocarbons 1,2,4-trimethylbenzene is present in the largest amount. Of C<sub>10</sub> aromatics, tetramethylbenzenes are present

in the largest amount (1.08% on the ligroin), and of these 1,2,3,5-tetramethylbenzene predominates (0.83% on the ligroin). Table 4 indicates that among six-membered naphthenes there are considerable amounts of propylcyclohexane (1.08% on the ligroin) and isopropylcyclohexane (0.63%). Among the ethylmethylcyclohexanes, as also in the case of the aromatic hydrocarbons, there is most of the hydrocarbons with the groups in the m-position, and among the trimethylcyclohexanes there is again a predominance of the hydrocarbon with the methyl groups in the 1,2,4-position (0.37%). Ethyldimethylcyclohexanes and tetramethylcyclohexanes correspond in content to less than the amounts in the aromatics. As regards cyclopentanes and paraffins, it follows from Table 5 that the amount of paraffins is about 1.5 times as great as the amount of naphthenes.

According to their boiling points, Fractions I, VII, and XII should contain mainly normal hydrocarbons, namely nonane, decane, and undecane. It will be seen from Table 5 that the content of normal hydrocarbons is one-third that of isoparaffins. On the assumption that in the composition of the high-boiling fractions isoparaffins are distributed approximately as in the gasoline, the relatively high yields of Fractions V, VI, X, and XI may indicate the presence in them of comparatively large amounts of mono- and di-substituted isoparaffins, with a predominance of the former.

TABLE 3

Hydro-carbon	Content in ligroin, %	Propyl-benzene	$d_4^{20}$	$n_D^{20}$	$R_A$	$R_N$
I	150 —163	2,36	0,8677	1,4930	0,96	
II	163 —167	0,47	0,8707	1,4955	0,97	0,08
III	167 —174	0,71	0,8745	1,4966	0,93	0,17
IV	174 —179	0,80	0,8720	1,4945	0,94	0,15
V	179 —182,5	0,62	0,8679	1,4840	0,96	0,08
VI	182,5—191	0,62	0,8721	1,4952	0,95	0,13
VII	191 —195	0,76	0,8736	1,4966	0,96	0,14
VIII	195 —200	1,07	0,8759	1,4988	0,94	0,21
	o-Ethyltoluene	3,27				
	m-Ethyltoluene	0,12				
	p-Ethyltoluene	10,80				

TABLE 4

Fraction	Content in ligroin (%)	Fraction	Content in ligroin (%)
1-Ethyl-2-methylcyclohexane	0.04	Butylcyclohexane	0.41
1-Ethyl-3-methylcyclohexane	0.52	1-Ethyl-3,5-dimethylcyclohexane	0.15
1-Ethyl-4-methylcyclohexane	0.28	4-Ethyl-1,2-dimethylcyclohexane	0.17
Propylcyclohexane	1.08	2-Ethyl-1,3-dimethylcyclohexane	0.07
Isopropylcyclohexane	0.63	2-Ethyl-1,4-dimethylcyclohexane	0.07
1,3,5-Trimethylcyclohexane	0.02	1-Ethyl-2,3-dimethylcyclohexane	Traces
1,2,4-Trimethylcyclohexane	0.37	1,2,3,5-Tetramethylcyclohexane	0.07
1,2,3-Trimethylcyclohexane	0.24	1,2,3,4-Tetramethylcyclohexane	0.07
s-Butylcyclohexane	0.24	1,2-Diisopropylcyclohexane	0.07
1-Isopropyl-4-methylcyclohexane	0.15	1,3-Diisopropylcyclohexane	Traces
Diethylcyclohexane	Traces	1,3-Diethylcyclohexane	0.02
Hexahydroindan	0.04	Identified	5.38
1-Methyl-3-propylcyclohexane	0.41	Not identified	2.03
1-Methyl-4-propylcyclohexane	0.26		

TABLE 5

Fraction	Boiling limits °C	Content in ligroin, %	$d_4^{20}$	$n_D^{20}$	Content, % on ligroin of	
					naphthenes	paraffins
I	149 —153	6,37	0,7408	1,4146	1,59	4,78
II	153 —157	1,98	0,7483	1,4170	0,67	1,31
III	157 —162,5	5,06	0,7510	1,4193	2,07	2,99
IV	162,5—166	3,08	0,7569	1,4222	1,13	1,95
V	166 —170	4,84	0,7563	1,4219	1,94	2,90
VI	170 —172	3,08	0,7526	1,4196	1,23	1,85
VII	172 —175	5,28	0,7535	1,4202	2,16	3,12
VIII	175 —179	3,96	0,7570	1,4226	1,23	2,73
IX	179 —184	3,74	0,7668	1,4268	1,87	1,87
X	184 —190	4,40	0,7750	1,4285	3,43	0,97
XI	190 —194	4,18	0,7635	1,4260	0,88	3,30
XII	194 —197	2,86	0,7617	1,4253	0,91	1,95
XIII	197 —200	2,42	0,7716	1,4290	1,18	1,24
	Residue	5,72				
	Losses	7,03				
Total		64,00			20,25	31,00

From the spectra given in the figure it is seen that the contents of trisubstituted derivatives of aromatic hydrocarbons decrease in the order 1,2,4; 1,2,3; 1,3,5.

#### SUMMARY

1. It was shown that the ligroin contained 26 aromatic, 26 cyclohexane, and 3 normal paraffin hydrocarbons.
2. The individual composition of the ligroin from Shurugin petroleum differs from that of the ligroins of Devonian petroleum in the relatively large content of cyclopentanes and of isoparaffins.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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## COMPOSITION OF THE BUTENES FORMED IN THE CATALYTIC DEHYDRATION OF 2-BUTANOL

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The question of the relative amounts of butene isomers formed in the heterogeneous catalytic dehydration of 2-butanol is of interest for the interpretation of the mechanism of asymmetric catalysis [1-4]. To determine the composition of the butenes we have carried out experiments on the dehydration of 2-butanol over a copper-quartz catalyst and over alumina, with chromatographic analysis of the butenes formed\*. There is a fairly large number of papers on the heterogeneous catalytic dehydration of n-butanols over alumina [5]. However, with the development of the gas-chromatographic method of analysis, it was only comparatively recently that studies were begun on the cis-trans isomerization of the butenes formed in the dehydration of alcohols.

In the dehydration of 1-butanol (or 2-butanol) a mixture of butenes is formed, namely 1-butene and cis- and trans-2-butenes, and with increase in time of contact their concentrations approach equilibrium values [6]. Preliminary treatment of the catalyst has a substantial effect on the composition of the mixture of butenes. Over alumina treated with potassium or sodium vapor or with gaseous ammonia, with short times of contact 1-butene gives the thermodynamically less stable cis-isomer instead of trans-butene. Similar stereospecificity with formation of the cis-isomer is observed also in the dehydration of the alcohol [7]. With increase in the time of contact the content of cis-isomer passes through a maximum and approaches the equilibrium value. With prolonged contact skeletal isomerization occurs with formation of small amounts of isobutene. The stereospecific formation of the cis-isomer is observed not only over alumina, but also over the catalysts  $\text{SiO}_2\text{-Al}_2\text{O}_3$ ,  $\text{NiO-Cr}_2\text{O}_3$ , and the catalyst  $\text{SiO}_2\text{-Al}_2\text{O}_3$  irradiated with neutrons [8-10]. In liquid-phase dehydration with phosphoric acid there is again predominant formation of cis-2-butene [8-9].

These regularities in the stereospecific formation of the cis-isomer apply to constant temperatures in the range 190-350°. The temperature-dependence of this process had not been examined in detail. There is only a communication by Musaev and Zizin [11] regarding the composition of the butenes formed in the dehydration of 1-butanol and 2-butanol over alumina in the range 340-450°. In the dehydration of 1-butanol the mixture of butenes formed slowly approached the equilibrium composition on elevation of the dehydration temperature to 400° and quickly approached it above this temperature. In the dehydration of 2-butanol the composition of the butenes changes little with temperature. As the authors state [11], change in the composition of the butenes formed in the dehydration of n-butanols at various temperatures is not the result of the isomerization of the butenes formed, as was assumed earlier. The stereospecific formation of cis-butene [11] is to be explained [10] by a cyclic structure in the transition state and indicates the importance of the existence of the geometric factor in the interaction of the catalyst with the chemisorbed reacting molecule, which is in accord with the multiplet theory.

### EXPERIMENTAL

The dehydration of 2-butanol was carried out in a flow catalysis apparatus. The 2-butanol was passed into the reactor with the aid of an automatic spray feed. The liquid catalyzate was collected in a receiver cooled with water (10°), and the rate of liberation of gaseous reaction products was measured in a eudiometer. The experiment lasted for 30-40 minutes. When a steady state had been reached, samples of gas were taken for analysis. The original 2-butanol, which was prepared by the hydrogenation of butanone under pressure over Raney nickel, was rendered abso-

\* The carrying out of such experiments to get a more precise picture of the dehydration mechanism was discussed with R. Berwell (U.S.) during the All-Union Conference on Organic Catalysis in Moscow (November 1959).





Fig. 1. Chromatogram of the gaseous reaction products in the catalytic transformations of 2-butanol over copper-quartz at 550°: 1) 1-butene; 2) trans-2-butene; 3) cis-2-butene.

lute with metallic calcium and fractionated; b.p. 99.5-99.8° (755 mm);  $n_D^{20}$  1.3968;  $d_4^{20}$  0.8069. Copper and alumina were used as catalysts.

Copper-on-quartz catalyst was prepared by the application of copper nitrate to ground (40-50 mesh) crystals of dextrorotatory daufin quartz. The catalyst was dried at 210°, roasted at 500° in a stream of air, and reduced in a stream of hydrogen at 220°. The amounts were 0.3 g of copper on 15.7 g of quartz in a layer 10 mm in length; volume of catalyst 10 ml. Another copper catalyst was prepared in accordance with [12] by the precipitation of 20% copper sulfate solution with an equimolecular amount of NaOH. The treatment of the catalyst and the reduction conditions were the same as before. The catalyst amounted to 1.17 g, and length of layer was 5 mm. Alumina was prepared by the precipitation of aluminum nitrate with ammonia, drying, and roasting at 450°. The amount of catalyst was 2.7 g, and the length of the layer was 5 mm.

The gaseous reaction products were analyzed by the method of gas chromatography [3], which readily permitted the separation of butene isomers. As liquid phase we used 3,3'-oxydipropionitrile [13] or N,N-dimethylformamide supported on fire brick (grains 0.10-0.25 mm) washed free from iron with hydrochloric acid.

Fig. 1 shows the chromatogram for the analysis of butenes formed in the dehydration of 2-butanol over a copper-quartz catalyst at 550°.

**Dehydration of 2-Butanol over Alumina.** The dehydration of 2-butanol over alumina was carried out in the range 315-445°. The rate of feed of 2-butanol was 0.125 ml/min; the conversion was 20-40%. The reproducibility of experiments was satisfactory, which indicated that the activity of the catalyst was constant. Table 1 gives the results of experiments on the relation of the composition of the butenes to temperature in the dehydration of 2-butanol. In Fig. 2 these results are represented graphically in the coordinates concentration and temperature. Fig. 2 shows that the content of 1-butene scarcely changes with temperature. The

TABLE 1. Temperature-dependence of the Composition of Butenes (% by vol.) Formed in the Dehydration of 2-Butanol over Alumina

Temp., °C	1-Butene	2-Butene		trans-2-Butene	cis-2-Butene	trans : cis
		trans-	cis-			
315,5	29,3	19,3	51,2	27,3	72,7	0,38
334	31,7	19,5	48,7	28,5	71,5	0,39
344,7	33,1	21,3	45,0	32,2	67,8	0,47
362,6	28,4	21,8	49,6	30,5	69,5	0,44
400	31,6	26,6	41,7	38,9	61,1	0,63
400	33,0	28,6	38,3	42,7	57,3	0,74
403	31,6	28,1	40,3	41,0	59,0	0,69
410	29,8	26,9	43,1	38,4	61,1	0,62
444	29,8	33,1	37,0	47,2	52,8	0,89
444	29,5	33,1	37,3	47,0	53,0	0,88

content of cis-2-butene falls from 72.7% at 315° to 53% at 440°, and the content of trans-2-butene rises correspondingly from 27.3% to 47%. In the temperature range investigated the content of cis-2-butene exceeds that of trans-2-butene; with rise in temperature their concentrations approach the equilibrium values (the broken lines in Fig. 2 are plotted from the data of [14,15]). A threefold increase of the time of contact  $\tau$  at 345° has little effect on the proportions of the butenes (Table 2, Fig. 3), though there is a tendency for an approach to equilibrium concentrations. No skeletal isomerization of the butenes occurs: isobutene was not detected. By-products (methane and propene) were formed in small amounts, but only at high temperatures.

**Dehydration of 2-Butanol over Copper Catalysts.** The dehydration of 2-butanol over the copper-quartz catalyst was carried out in the range 550-590°. The rate of feed of 2-butanol was 0.12 ml/min, and the conversion was 30-50%. The dehydration in experiments carried out at a higher temperature (570-588°) attained 10-20% of the total conversion. Dehydration at high temperatures was accompanied by the formation of considerable amounts of methane, ethane, and ethylene. The complete analysis of gas from experiments carried out with various times of contact is



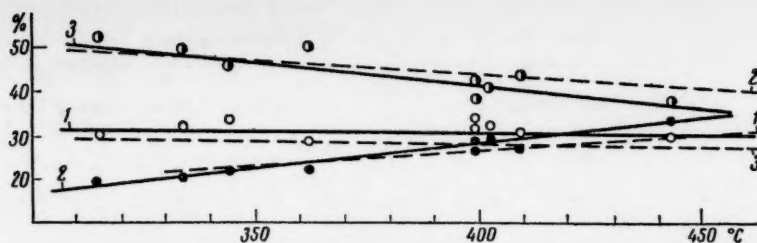


Fig. 2. Relation of the composition of butenes formed in the dehydration of 2-butanol over alumina to temperature: 1) 1-butene; 2) trans-2-butene; 3) cis-2-butene (broken lines: equilibrium concentrations plotted from [14,15]).

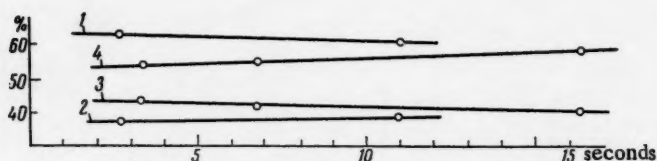


Fig. 3. Relation of the compositions of butenes formed (%) to the time of contact (sec) in the dehydration of 2-butanol over alumina [1) cis-2-butene; 2) trans-2-butene] and over copper-quartz [3) cis-2-butene; 4) trans-2-butene].

TABLE 2. Relation of the Composition of Butenes (% by vol.) to Time of Contact (dehydration of 2-butanol over alumina at 344.7°)

Time (sec)	1-Butene	2-Butene		trans-2- Butene	cis-2- Butene	trans : cis
		trans-	cis-			
10,9	31,7	26,7	41,6	39,1	60,9	0,64
2,7	33,5	23,8	42,5	35,8	64,2	0,55

given in Table 3; Table 4 gives data on the temperature-dependence of the composition of the butenes. It must be mentioned that, as experiment showed, pure quartz does not bring about appreciable decomposition of 2-butanol in the range of temperatures investigated.

It will be seen from Table 4 and Fig. 4 that with rise in dehydration temperature the content of 1-butene does not remain constant, as in the case of alumina, but diminishes. Over the whole range of temperatures investigated the content of trans-isomer exceeds that of the cis-isomer, and their concentrations approach the equilibrium values (broken lines in Fig. 4).

Further experiments were carried out to determine the possibility of the occurrence of the thermal and catalytic isomerization of the butenes formed under conditions close to that for the dehydration of 2-butanol. Thermal isomerization was studied for a mixture of butenes containing 48.7% of the cis-isomer. The mixture was passed over quartz powder (30-50 mesh) at 550° with a time of contact of 52 seconds, which is 8-9 times as great as the time of contact in the usual experiments on the decomposition of 2-butanol over copper. Even under these conditions, which were more favorable for isomerization, the content of the trans-isomer was increased by only 3.2% (Table 5). On passage of the same mixture of butenes over the copper-quartz catalyst at 550° with a time of contact of 4.4 seconds, isomerization of the cis-isomer into the trans-isomer amounted to 3.9%, and on increase in the time of contact eightfold the isomerization attained 4.8% (Table 6). Change in the time of contact in the dehydration reaction has little effect on the composition of the butenes. A fivefold change in the time of contact raises the content of the trans-isomer by only 1.6% (Table 7, Fig. 3).

TABLE 3. Relation of the Composition of the Gaseous Dehydration Products of 2-Butanol (% by vol.) over a Copper-Quartz Catalyst to the Time of Contact (550°)

Time (sec)	H <sub>2</sub>	Methane	Ethane	Ethylene	Propane	Propene	Butane	Butenes
3,3	49,5	25,9	4,2	6,50	0,5	3,6	—	10,1
6,7	54,5	21,5	3,9	6,2	3,1	—	—	10,6
16,3	21,9	29,9	10,9	10,9	—	3,5	—	23,8

TABLE 4. Temperature-dependence of the Compositions of Butenes (% by vol.) Formed in the Dehydration of 2-Butanol over a Copper-Quartz Catalyst. (Rate of feed 0.12 ml/min; time of contact  $\tau$  6-7 sec.)

Temp., °C	1-Butene	2-Butene		trans-2-Butene	cis-2-Butene	trans : cis
		trans-	cis.			
550	42,1	33,8	24,0	58,4	41,6	1,40
550	—	—	—	58,0	42,0	1,38
560	38,6	34,0	27,3	55,4	44,6	1,24
570	39,2	35,2	25,4	58,0	42,0	1,38
588	36,3	38,5	25,0	60,6	39,4	1,53

TABLE 5. Change of Composition (% by vol.) in the Thermal Isomerization of Butenes. (Quartz catalyst, grains 30-50 mesh; 550°;  $\tau$  52 sec)

Material	1-Butene	2-Butene		trans-2-Butene	cis-2-Butene	trans:cis
		trans-	cis-			
Original mixture	31.7	19.5	48.7	28.5	71.5	0.39
Isomerization product	31.1	22.7	46.1	32.9	67.1	0.49

TABLE 6. Relation of the Change in Composition (% by vol.) in the Catalytic Isomerization of Butenes over a Copper-Quartz Catalyst (550°) to the Time of Contact ( $\tau$ )

Material	Time (sec)	1-Butene	2-Butene		trans-2-Butene	cis-2-Butene	trans:cis
			trans-	cis-			
Original mixture		33.5	23.8	42.5	35.8	64.2	0.56
Isomerization product	4.4	28.5	27.7	43.5	38.9	61.1	0.63
Original mixture		31.7	26.7	41.6	39.1	60.9	0.64
Isomerization product	39	38.3	31.5	30.2	51.0	49.0	1.04

As the copper-quartz catalyst contained only a small amount of metal and brought about no dehydration below 500°, we investigated a catalyst prepared according to the directions of Hara and others [12]. The dehydration of 2-butanol over this catalyst was carried out in the range 450-570°. The composition of the gaseous reaction products is given in Table 8. It will be seen that this catalyst brings about the decomposition of 2-butanol to lower hydrocarbons to a considerably less extent than copper on quartz (cf. Table 3). At the same time, the extent of the dehydration was only slightly less than that obtained with the copper-quartz catalyst; in the latter the carrier, quartz, has a certain effect.

The temperature-dependence of the contents of butenes is shown in Fig. 5. It will be seen that the statement of Hara and others [12] concerning the exclusively dehydrating character of the copper catalyst prepared by the precipitation of a solution of copper sulfate with an equimolecular amount of alkali is not confirmed with respect to 2-butanol: only at 570° did the content of butenes attain 10-12%. The rest of the product consisted of hydrogen (and methane?) and small amounts (1-1.5%) of propene.

TABLE 7. Relation of the Composition of Butenes Formed in the Dehydration of 2-Butanol over a Copper-Quartz Catalyst (550°) to Time of Contact

Temp., °C	1-Butene	2-Butene		trans-2- Butene	Cis-2- Butene	trans : cis
		trans-	cis-			
3,3	41,3	32,6	26,1	55,5	44,5	1,24
6,7	—	—	—	57,3	42,7	1,34
16,3	41,3	34,2	24,6	58,1	41,9	1,38

TABLE 8. Temperature-dependence of the Composition of the Products of the Reaction of 2-Butanol over a Copper Catalyst (prepared from CuSO<sub>4</sub> by Hara's method [12])

Temp°C	H <sub>2</sub> , CH <sub>4</sub>	Propene	1-Butene	2-Butene		trans-2- Butene	cis-2- Butene	trans : cis
				trans-	cis-			
450	97,5	0,43	0,89	0,41	0,66			
			45	20,9	33,6	38,3	61,7	0,62
530	97,1	0,36	1,0	0,88	0,60			
			38,7	34,1	23,2	59,5	40,5	1,46
550	90,6	1,2	3,5	2,6	1,9			
			43,7	32,5	2,37	58,1	41,9	1,38
570	85,3	2,6	4,9	4,28	2,81			
			40,8	35,6	23,4	60,3	39,7	1,51

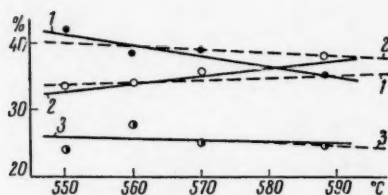


Fig. 4. Temperature-dependence of the composition of butenes formed in the dehydration of 2-butanol over copper-quartz: 1) 1-butene; 2) trans-2-butene; 3) cis-2-butene (the broken lines refer to equilibrium concentration and are plotted in accordance with [14,15]).

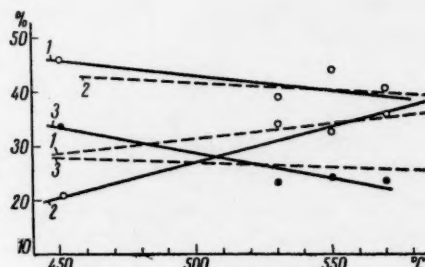
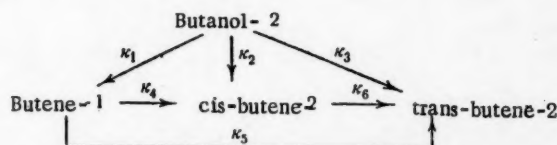


Fig. 5. Relation of the composition of the butene on the temperature of the dehydration of 2-butanol over a copper catalyst prepared in accordance with [12]: 1) 1-butene; 2) trans-2-butene; 3) cis-2-butene (broken lines: equilibrium concentrations according to [14,15]).

#### DISCUSSION OF EXPERIMENTAL RESULTS

The data obtained are concerned with the important question of the mechanism of the dehydration of 2-butanol and the isomerization of the butenes. Actually, until the mechanism of the dehydration of 2-butanol has been elucidated, it is impossible to make a firm assertion that the butenes formed in the reaction arise exclusively in the dehydration stage and not in an accompanying isomerization stage. The possible ways in which the process may proceed are presented in the following scheme:



In this, if the composition of the butenes is determined by the dehydration reaction, then  $k_1$ ,  $k_2$  and  $k_3 > k_4$ ,  $k_5$ , and  $k_6$ ;

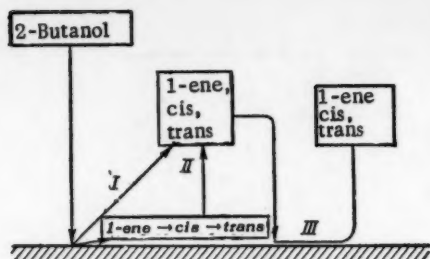


Fig. 6. Scheme of possible mechanism of the catalytic dehydration of 2-butanol.

From the experimental material examined it follows that stage III can probably be excluded in as much as a) a mixture of butenes with a large content of the less stable butenes (1-butene and cis-2-butene) is not isomerized to an appreciable extent over a copper catalyst under the experimental conditions; only when the time of contact is increased considerably does isomerization attain 10%; b) the composition of the butenes varies little with the coverage of the catalyst surface.

To make a choice between processes I and II is considerably more difficult in that both processes proceed in the activated state on the catalyst surface. Scheme I is favored by the fact that the effect of the hydrogen in whose presence isomerization occurs is insignificant in our experiments: the composition of the butenes changes regularly toward the equilibrium concentrations on rise in the reaction temperature. This occurs both over a purely dehydrating catalyst such as alumina and over a copper catalyst which promoted both reactions, dehydration and dehydrogenation, i.e., in presence of hydrogen. With the object of confirming this mechanism it is planned to carry out a radiochemical investigation.

#### SUMMARY

1. By the method of gas-liquid chromatography a study was made of the composition of the butenes formed in the dehydration of 2-butanol over alumina (315-445°) and over copper catalysts (450-590°).
2. Over alumina cis-2-butene is formed preferentially, and over a copper catalyst there is preferential formation of trans-2-butene.
3. An examination was made of the possible mechanism of the catalytic dehydration of 2-butanol and the formation of isomeric butenes.

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# CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS AND THEIR HYDROPOLYMERIZATION UNDER THE ACTION OF CARBON MONOXIDE AND HYDROGEN

COMMUNICATION 33. FORMATION OF HIGHER HYDROCARBONS WITH A NON-  
MULTIPLE NUMBER OF CARBON ATOMS WITH RESPECT TO THE ORIGINAL OLEFIN

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,  
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In the catalytic hydropolymerization of olefins under the action of carbon monoxide in presence of hydrogen and in the hydrocondensation of carbon monoxide with olefins, on the one hand true polymers and their hydrogenation products are formed, and on the other hydrocarbons with nonmultiple numbers of carbon atoms with respect to the olefin are formed. Thus, in the higher-boiling part of the condensate containing hydrocarbons with more carbon atoms than the original olefin, in the case of ethylene there are found (% by weight) 7.4 C<sub>3</sub> hydrocarbons; 19.6 C<sub>4</sub>; 7.8 C<sub>5</sub>; 12.9 C<sub>6</sub>; 11.8 C<sub>7</sub>; 9.7 C<sub>8</sub>; 6.7 C<sub>9</sub>; 24.1 higher; in all 33.7% of hydrocarbons with a nonmultiple of carbon atoms [1]; in experiments with propene: 5.0 C<sub>4</sub>; 12.6 C<sub>5</sub>; 18.6 C<sub>6</sub>; 13.7 C<sub>7</sub>; 12.4 C<sub>8</sub>; 11.7 C<sub>9</sub>; 26.0% higher; in all 43.7% of hydrocarbons with a nonmultiple of carbon atoms [2]. In these experiments we started with a mixture containing 5-6% of CO and olefin and hydrogen in the ratio of 1 : 1. In the case of 1-butene with an analogous mixture the higher-boiling part of the condensate contained 23.2 C<sub>5</sub>; 26.0 C<sub>6</sub>; 13.3 C<sub>7</sub>; 11.2 C<sub>8</sub>; 10.0 C<sub>9</sub>; 16.3% higher hydrocarbons; in all 72.5% of hydrocarbons with a nonmultiple of carbon atoms [1]. In experiments with 1-butene at a ratio of olefin: hydrogen of 3 : 1, the total amount of hydrocarbons with a nonmultiple of carbon atoms was approximately the same (73.6%), but the content of hydrocarbons of higher molecular weight increased: the higher-boiling part of the condensate contained 8.0 C<sub>5</sub>; 10.3 C<sub>6</sub>; 10.4 C<sub>7</sub>; 10.0 C<sub>8</sub>; 3.6 C<sub>9</sub>; 11.5 C<sub>10</sub>; 6.7 C<sub>11</sub>; 7.1 C<sub>12</sub>; 7.0 C<sub>13</sub>; 6.1 C<sub>14</sub>; 5.0 C<sub>15</sub>; 7.4 C<sub>16-17</sub>; 5.0 C<sub>18-19</sub>; 1.9% of higher.

From 1 : 1 a mixture of 1-octene and hydrogen containing 6% of CO we obtained a condensate the higher-boiling part of which contained 7.9 C<sub>9</sub>; 20.7 C<sub>10</sub>; 14.1 C<sub>11</sub>; 11.7 C<sub>12</sub>; 2.6 C<sub>13</sub>; 4.6 C<sub>14</sub>; 5.3 C<sub>15</sub>; 5.9 C<sub>16</sub>; 8.0 C<sub>17</sub>; 5.5 C<sub>23</sub>; 13.7 C<sub>48</sub>. The amount of hydrocarbons with a nonmultiple of carbon atoms with respect to the original olefin was about 85% [4].

The multiplicity of a hydrocarbon K<sub>i</sub> is defined by the equation

$$K_i = \frac{n_i}{n}, \quad (1)$$

in which n<sub>i</sub> is the number of carbon atoms in the molecule of the *i*th hydrocarbons and *n* is the number of carbon atoms in the original olefin. For a true polymer K<sub>i</sub> is a whole number, but for a hydrocarbon with a nonmultiple of carbon atoms it is an improper fraction. The mean multiplicity K<sub>m</sub> of the whole of the higher-boiling part of the condensate (containing hydrocarbons in which the number of carbon atoms is greater than *n*) is defined by the equation

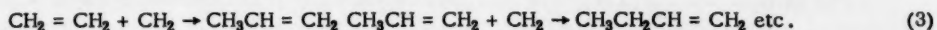
$$K_m = \sum a_i K_i = \frac{1}{n} \sum a_i n_i, \quad (2)$$

in which a<sub>i</sub> is the fraction of the *i*th hydrocarbon in the higher-boiling part of the condensate.

The mean multiplicity of the higher-boiling part of the condensate obtained from a 1 : 1 mixture of olefin and hydrogen containing 5-6% of CO has the following values: for ethylene 3.9, propene 2.9, 1-butene 2.2, 1-octene 1.8; for 1-butene in a 3 : 1 1-butene-hydrogen mixture it is 2.5.

From the data cited it will be seen that with rise in the molecular weight of the original olefin there is an increase in the content of hydrocarbons with nonmultiple numbers of carbon atoms in the higher-boiling part of the condensate and reduction in the mean multiplicity  $K_M$ . Increase in the yield of hydrocarbons with nonmultiplicities of carbon atoms as the molecular weight of the original olefin rises is to be explained by the fact that the greater the number of carbon atoms in the molecule, the greater the number of such hydrocarbons that are possible. In fact, the number of such hydrocarbons possible in a row, e.g., between two neighboring true polymers, is  $n - 1$  for any olefin  $C_nH_{2n}$ , i.e., increases with increase in the number of carbon atoms in the molecule of this olefin.

In examining the ways of formation of higher hydrocarbons with nonmultiples of carbon atoms we must point out that they cannot be formed in such a large amount by the hydrocracking of the original olefin or by its hydrocondensation with carbon monoxide in accordance with the scheme



Actually, in experiments with binary mixtures of olefin and hydrogen (in absence of carbon monoxide) the yield of condensate, though increasing with rise in the molecular weight of the original olefin, was very small and amounted to (% by weight on original olefin) 0.0 for ethylene, 1.9 for propene, 2.1 for 1-butene, 7.6 for 1-hexene, and 7.7 for 1-octene [4,5]. As regards hydrocondensation (Equation (3)), by this way note more than 5-15% of higher hydrocarbons could be formed [6].

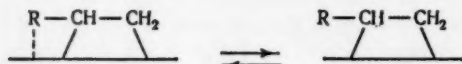
The suggestion [7] of the dissociation of ethylene into methylene radicals in the course of its hydropolymerization under the action of carbon monoxide in presence of hydrogen has as yet no experimental support.

There remains the view that the formation of hydrocarbons with a nonmultiple of carbon atoms with respect to the original olefin is due to the rupture of carbon-carbon bonds in the course of the process itself with subsequent reaction of the radicals formed. We must point out that the number of molecules of the original  $\alpha$ -olefin of normal structure entering this reaction of the formation of higher hydrocarbons for each carbon monoxide molecule that reacts (yield on the initiator) falls with increase in the molecular weight of the olefin for given reaction conditions. Thus, with ratios in the original gas of  $[H_2]/[CO] \sim 8$  and  $[C_nH_{2n}]/[H_2] \sim 1$ , the yield on the initiator is: for ethylene 6-8, for propene  $\sim 4$ , for 1-butene  $\sim 3$ , and for 1-hexene  $\sim 2$  [8]. Thus, for each carbon monoxide molecule that reacts, a number of olefin molecules react such that the total number of carbon atoms in them is about 12, irrespective of the molecular weight of the olefin. In other words, the yield on the initiator expressed as the number of carbon atoms is a constant under given conditions of reaction and given concentrations of the reactants. The constancy probably indicates that all these carbon atoms are reacting atoms and are therefore adsorbed by the catalyst surface. It follows that the hydrocarbon chains formed are adsorbed in the flat position on the catalyst and are deformed with the result that in the reaction there is ready rupture of carbon-carbon bonds with formation of surface radicals. The rupture of C-C bonds with formation of radicals is confirmed by the occurrence of chain-transfer in the reaction, which is indicated by the fact that the number of carbon atoms expressing the yield on the initiator is greater than the mean number of carbon atoms in terminal hydrocarbons (the molecular chain). The radicals so formed on the catalyst surface react with adsorbed olefin molecules forming hydrocarbons with nonmultiples of carbon atoms. In these processes, however, an important part is played by the products of the incomplete reduction of carbon monoxide, for we have found that in absence of carbon monoxide such reactions occur to an extremely small extent or do not go at all, as in the case of ethylene.

Hence, in the catalytic transformations of olefins under the action of carbon monoxide in presence of hydrogen the growth of hydrocarbon chains proceeds not so much by the interaction between molecules of the original olefin, as between them and radicals formed by the rupture of carbon-carbon bonds, as a result of which hydrocarbons with a nonmultiple of carbon atoms predominate in the higher-boiling reaction products. To a small extent there are formed also some hydrocarbons with fewer carbon atoms than the original olefin.

The flat adsorption of olefin molecules, considered above, occurs at low carbon monoxide concentrations under conditions of radical-chain growth of the hydrocarbon chain. At high carbon monoxide concentrations in the original gas we may have adsorptional displacement of carbons of the olefin which do not stand at the double bond by carbon monoxide. Olefin molecules are then adsorbed only by the carbon atoms at the double bond without

deformation. Under these conditions the hydrocarbon chain may grow without the rupture of carbon-carbon bonds by the hydrocondensation of olefin with carbon monoxide (Reaction (3)). It follows that, depending on the carbon monoxide and hydrogen contents of the original mixture and the tendency of the olefin to be adsorbed, one form of adsorption of an olefin molecule may pass into the other, and the direction of the reaction



will change accordingly. Such mutual transitions of the reactions of olefins under the action of carbon monoxide and hydrogen has been observed by us in practice and will be described in greater detail in the next communication.

#### SUMMARY

1. The yield of higher hydrocarbons with nonmultiple numbers of carbon atoms with respect to the original olefin formed in the reaction of olefins under the action of carbon monoxide and hydrogen increases with rise in the molecular weight of the original  $\alpha$ -olefin with reduction in the mean multiplicity of the higher-boiling part of the condensate.
2. The formation of such hydrocarbons is due mainly to rupture of carbon-carbon bonds with formation of surface radicals that interact with the original olefin.
3. The rupture of carbon-carbon bonds is facilitated by the flat disposition of the adsorbed olefin molecule on the catalyst surface.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE  
WITH OLEFINS AND THEIR HYDROPOLYMERIZATION UNDER  
THE ACTION OF CARBON MONOXIDE AND HYDROGEN

COMMUNICATION 34. MUTUAL TRANSITIONS OF THE REACTIONS OF THE FORM-  
ATION OF HYDROCARBONS FROM MIXTURES OF ETHYLENE, HYDROGEN AND CAR-  
BOND MONOXIDE

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We have previously [1] advanced the view that at one of the stages of the synthesis of higher hydrocarbons from carbon monoxide and hydrogen there is occurring the free-radical reaction of the hydrocondensation of carbon monoxide with olefins, but at subsequent stages there may occur a transition from this reaction to the hydropolymerization of olefins, which, as has been shown, has a radical-chain character. One of the criteria by which one may judge whether a radical-chain reaction predominates is a yield on the initiator of more than unity, though such a reaction may proceed with any value of yield.

In the present work we determined the possibility of such mutual transitions of these reactions over a catalyst active both in the Orlov-Fischer-Tropsch reaction and in the hydropolymerization of olefins and their hydrocondensation with carbon monoxide. As the usual hydropolymerization and hydrocondensation catalyst Co-clay [2] is less active in the synthesis of hydrocarbons from CO and H<sub>2</sub> and the classical catalyst for this reaction Co-ThO<sub>2</sub>-kieselguhr is insufficiently active in reactions in which olefins participate [3], we made an attempt to prepare a catalyst that was equally active in all these processes, which we managed to achieve by promoting a Co-clay catalyst with an addition of 18% of ThO<sub>2</sub> (calculated on the metallic cobalt), as also in the case of a Co-kieselguhr catalyst.

EXPERIMENTAL

The catalyst was prepared by the previously described method [2]. The experiments were carried out at atmospheric pressure and 190° in a flow system at a space velocity of the original gas mixture of close to 100 hr<sup>-1</sup>. The apparatus and experimental procedure did not differ from those described previously [1-3]. The catalyst, volume 30-33 ml, was loaded into a Pyrex reaction tube, internal diameter 12 mm, and was reduced with hydrogen at 450° for five hours. Regeneration after prolonged work was carried out in the same way. We used the original mixture 1CO : 2H<sub>2</sub> and ternary C<sub>2</sub>H<sub>4</sub>-H<sub>2</sub>-CO mixtures of various compositions. The experimental results are given in Tables 1-3 and in Fig. 1.

In Table 1 the yields of liquid hydrocarbons are expressed in milliliters per cu.m of original mixture, and in experiments with ternary mixtures the calculation was made on the sum of the amounts of all three components. Table 2 gives the volumes and compositions of the original and final gases, and Table 3 gives the extent to which each component takes part in the formation of liquid hydrocarbons, calculated on its original amount, and also the yields of ethane formed from the original C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub>. Table 3 gives the molar proportions of CO, H<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub> entering the same reaction, the number of moles of CO entering the reaction being taken as unity. Hence the two numbers following unity express the ratios (H<sub>2</sub>/CO)<sub>c</sub> and (C<sub>2</sub>H<sub>4</sub>/CO)<sub>c</sub>, the numbers of moles of H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> entering the reaction of the formation of higher hydrocarbons for every mole of CO entering the same reaction. The second ratio (C<sub>2</sub>H<sub>4</sub>/CO)<sub>c</sub> coincides with the quantity that we have previously referred to as "yield on the initiator" [1]. To obtain all these ratios it was necessary to calculate the amounts of H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> entering the reaction of the hydrogenation of ethylene to ethane and the amount of CO converted into CO<sub>2</sub>. In Table 3, for the purposes of comparison we give



TABLE 1.

Catalyst	Expt	Duration of expt., hr	Mean space velocity of gas, hr <sup>-1</sup>	Gas concentration	Average yield (ml/cu·m)			
					Heavy oil (H)	Light oil (L)	H + L	Reaction water
1	1***	5	83	67,1	0,0	0,0	0,0	109,5
1	2*	20	82	67,6	77,3	60,8	138,1	162,2
1	3***	5	91	62,9	0,0	0,0	0,0	99,5
2	4**	5	75	71,5	129,2	155,1	284,3	120,7
2	5	20	86	57,3	89,7	126,5	216,2	93,4
2	6**	5	94	77,4	191,8	479,4	671,2	13,7
2	7	20	94	74,5	152,0	461,7	613,7	34,2
2	8	5	86	37,3	48,5	111,9	160,4	67,0

\*Experiment with the mixture: 66.3% H<sub>2</sub> + 29.7% CO.

\*\* Before this experiment the catalyst was reduced (or regenerated) with hydrogen.

TABLE 2.

Expt.	Original gas				Final gas					
	Vol. (liters)	Comp. (% by vol.)			vol. (liters)	Comp. (% by vol.)				
		CO	H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>		CO	H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO <sub>2</sub>
4	11,6	25,1	45,7	29,2	3,3	15,2	33,3	3,0	42,5	6,0
5	53,4	24,3	48,1	27,6	22,8	24,1	35,0	13,1	26,2	1,6
6	14,6	6,9	39,0	54,1	3,3	3,0	27,3	6,0	63,7	0,0
7	58,1	7,6	39,4	53,0	14,8	4,7	24,2	13,4	56,4	1,3
8	13,4	34,3	31,4	34,3	8,4	34,6	22,6	33,4	7,1	2,3

TABLE 3.

Expt.	Amt. reacting to form liquid hydrocarbons (% on reactant)			C <sub>2</sub> H <sub>6</sub> formed, % on original		Molar proportions CO: H <sub>2</sub> : C <sub>2</sub> H <sub>4</sub>	
	CO	H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	reacting to form liquid hydrocarbons	in original gas
4	75,9	52,8	55,8	26,4	41,2	1:1,3:0,86	1:1,8:1,2
5	55,0	45,5	38,7	23,3	40,8	1:1,6:0,8	1:2,0:1,1
6	90,0	47,3	70,9	36,8	26,6	1:3,0:6,2	1:5,6:7,8
7	79,5	47,6	66,2	36,6	27,2	1:3,1:5,8	1:5,2:7,0
8	32,6	40,5	26,0	14,3	13,0	1:1,1:0,8	1:0,9:1,0

also the molar proportions of the three components in the original gas. As in this case also CO was taken as unit, the numbers following unity may be denoted by the expressions (H<sub>2</sub>/CO)<sub>or</sub> and (C<sub>2</sub>H<sub>4</sub>/CO)<sub>or</sub>. In Fig. 1 experiments after which the catalyst was regenerated are marked by a broken vertical line

Experiments on the Synthesis of Hydrocarbons from CO and H<sub>2</sub> were carried out with two samples of catalyst. As the results obtained with the two samples were exactly the same, data are given for experiments with one of them (Experiments 1-3, Table 1, Curve 1, Fig. 1). First of all it must be stated that in the first 5-7 hours of work, immediately after the reduction of the catalyst, liquid hydrocarbons were not formed at all, but the main reaction products in this stage were CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>O (Expt. 1). The same was observed after the regeneration of the catalyst (Expt. 3). In Fig. 1 this phenomenon is evidenced by the initial sections on Curve (1), which coincide with the axis of abscissae. Liquid hydrocarbons began to make their appearance in the reaction products only after 6-7 hours from the start of the work of the catalyst after reduction or regeneration (Expt. 2, Table 1), and the yield rose gradually with each cycle (from regeneration to regeneration), which will be seen on the sections (1), (1a), and (1c) on Curve (1), Fig. 1, and in the course of a given cycle the yield falls somewhat. The maximum yield of liquid hydrocarbons obtained



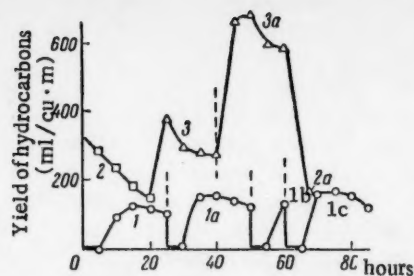
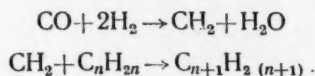


Fig. 1. Various types of reactions of the formation of hydrocarbons and their mutual transformations: 1, 1a, 1b, and 1c) synthesis of hydrocarbons from CO and H<sub>2</sub>; 2 and 2a) hydrocondensation of CO with C<sub>2</sub>H<sub>4</sub>; 3 and 3a) hydropolymerization of C<sub>2</sub>H<sub>4</sub> under the action of Co.

CO. At the lower concentrations of CO the yield of liquid hydrocarbons was 2-3 times as high as at the higher concentration, other conditions being equal.

However, the difference may have not only a quantitative, but also a qualitative character, in that two different processes are possible here: the hydropolymerization of ethylene under the action of small amounts of CO and the hydrocondensation of CO with ethylene. Actually, as can be seen from Table 3, at (H<sub>2</sub>/CO)<sub>or</sub> ~1-2 and (C<sub>2</sub>H<sub>4</sub>/CO)<sub>or</sub> ~1-1.6 the yield on the initiator (C<sub>2</sub>H<sub>4</sub>/CO)<sub>c</sub> is 0.8-0.9. This means that in the reaction leading to the formation of liquid hydrocarbons approximately one molecule of C<sub>2</sub>H<sub>4</sub> reacts for each molecule of CO. This reaction may be expressed in the general hydrocondensation scheme



Quite different relations are found in the other group of experiments. With (H<sub>2</sub>/CO)<sub>or</sub> ~5-6 and (C<sub>2</sub>H<sub>4</sub>/CO)<sub>or</sub> ~7-8 the yield on the initiator (C<sub>2</sub>H<sub>4</sub>/CO)<sub>c</sub> is 6. Hence, in the formation of hydrocarbons one reacting molecule of CO draws six molecules of ethylene into this reaction; this indicates that the hydropolymerization of ethylene under the action of small amounts of CO has a chain character. Hence, by change in the composition of the original gas in presence of a catalyst active in the synthesis of hydrocarbons from CO and H<sub>2</sub> we may bring about a transition from hydrocondensation to hydropolymerization and back. The latter was observed as we passed from Expt. 7 to Expt. 8 (Tables 1-3). In Expt. 8 one-third of the original gas was CO; nevertheless, there was no transition to the Orlov-Fischer-Tropsch reaction, and the process assumed the character of hydrocondensation. This follows from the fact that the yield on the initiator (C<sub>2</sub>H<sub>4</sub>/CO)<sub>c</sub>, as also in Experiments 4 and 5, was 0.8. Ethylene took active part in the formation of hydrocarbons, which, however, were obtained in lower yield than in Experiments 4 and 5 because of the fatigue of the catalyst, which was not regenerated before Expt. 8. In experiments with mixtures of C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>, and CO together with the formation of liquid hydrocarbons there was a simultaneous hydrogenation of ethylene to ethane. From a comparison of the yields of ethane in Experiments 4, 5 and 8 (Table 3) it will be seen that for a given value of (C<sub>2</sub>H<sub>4</sub>/CO)<sub>or</sub> of ~1 the yield of ethane was about 40% for (C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>)<sub>or</sub> ~0.5-0.6 (Experiments 4 and 5) and 13% for (C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>)<sub>or</sub> ~1 (Expt. 8).

Hence, the reduction of the ratio (C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>)<sub>or</sub> favors the hydrogenation of ethylene to ethane. In experiments 6 and 7 (C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>)<sub>or</sub> was 1.3-1.4. It might be expected that the yield of ethane would be less than in Expt. 8. Actually, it was twice as great, being 27%. This is probably to be explained by the fact that in Experiments 6 and 7 the ratio (C<sub>2</sub>H<sub>4</sub>/CO)<sub>or</sub> was about 7-8, whereas in Expt. 8 it was unity. This shows that in Expt. 8 the hydrogenation of ethylene to ethane was hindered by the relatively high concentration of CO.

after 75 hours of work was 165 ml/cu.m. The results show that the activity of the catalyst Co-ThO<sub>2</sub>-clay in the synthesis of higher hydrocarbons from CO and H<sub>2</sub> differs little from that of Co-ThO<sub>2</sub>-kieselguhr [4].

Experiments with Mixtures of C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>, and CO were carried out with a new freshly reduced portion of catalyst (Catalyst 2). A series of experiments was first carried out with gas mixtures containing 25% of CO (Experiments 4 and 4, Tables 1-3, Curve (2), Fig. 1), and then, without regeneration of the catalyst, with mixtures containing 7-7.5% of CO (Curve (3), Fig. 1; these experiments are not given in the table). Further, after regeneration of the catalyst we used mixtures in which the CO concentration was again 7-7.5% (Experiments 6 and 7, Table 1-3, Curve (3a), Fig. 1) and, finally, without regeneration of the catalyst we carried out Expt. 8 (Tables 1-3; (2a) in Fig. 1), in which the original gas had the maximum content of CO of 34.3%.

All the experiments carried out with mixtures of C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>, and CO may be divided into two groups: experiments with mixtures containing 7-7.5% of CO and experiments with an original gas containing 25-35% of

It should be noted that the molar proportions in which CO, H<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub> enter the reaction of the formation of liquid hydrocarbons are fairly close to the proportions of the gases in the original mixture. In fact, from Table 3 it is seen that approximately

$$(C_2H_4/CO)_{or} \approx (C_2H_4/CO)_c \text{ and } (H_2/CO)_{or} \approx (H_2/CO)_c$$

Particular attention is merited by the fact that, unlike the synthesis of hydrocarbons from CO and H<sub>2</sub>, hydro-polymerization and hydrocondensation proceed also in the first 5-7 hours of work after the reduction or regeneration of the catalyst. Moreover, it is just in this period of the so-called development of the catalyst that the yield of liquid hydrocarbons in these reactions is a maximum. This is readily seen from a comparison of Expt. 4 with Expt. 5 or of Expt. 6 with Expt. 7 (Table 1), and also from the character of the curves (2), (3), and (3a) in Fig. 1. From Fig. 1 it can be seen also that the catalyst is extremely readily activated by treatment with hydrogen. The intensity of the reactions involving C<sub>2</sub>H<sub>4</sub> with formation of higher hydrocarbons at the stage at which only methane is formed from CO and H<sub>2</sub> is an extremely interesting fact that undoubtedly has a direct connection with the above-noted increase in the yield on the initiator (C<sub>2</sub>H<sub>4</sub>/CO)<sub>c</sub> with increase in the ration (H<sub>2</sub>/CO)<sub>or</sub> and may be explained as follows.

It is known [5,6] that the formation of methane from CO and H<sub>2</sub> in the first hours of the work of a Co-ThO<sub>2</sub> catalyst is due to overheating of the catalyst caused by the high intensity of the exothermic reaction on the active surface. Methane formation gradually ceases as the catalyst becomes inactivated or immediately on dilution of the CO-H<sub>2</sub> mixture with nitrogen or methane. Herington and Woodward [7], who also explained the formation of CH<sub>4</sub> from CO and H<sub>2</sub> over a Co catalyst by insufficient lowering of the temperature after the reduction of the catalyst and too high a ratio (H<sub>2</sub>/CO)<sub>or</sub>, achieved a reduction in the concentration of hydrogen at the catalyst surface by partial poisoning of the latter with sulfur compounds. As a result, even at 300°, instead of the "methane reaction" the synthesis of liquid hydrocarbons from CO and H<sub>2</sub> proceeded. In a similar way, Craxford [8] obtained liquid hydrocarbons from CO and H<sub>2</sub> at 280° when the original mixture was diluted with ethylene, which partially displaced adsorbed hydrogen from the surface. It follows that of the factors favoring methane formation from CO and H<sub>2</sub>, both in the initial period of the "development" of a Co catalyst, and also under the usual conditions, the most powerful is the excess concentration of hydrogen on the catalyst; its artificial lowering enables one to obtain liquid hydrocarbons, even at 300°, the temperature characteristic for the "methane reaction".

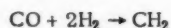
The synthesis of hydrocarbons from CO and H<sub>2</sub> has the character of a hydropolymerization and hydrocondensation reaction, as it may be regarded as established that the radicals formed by the reduction of carbon monoxide polymerize (methylene radicals) or condense, e.g., with elimination of water (hydroxymethylene radicals) [9]. It is evident that under the conditions for the "methane reaction" such processes, consisting in the reactions of radicals among themselves, become difficult, as a result of which their action is directed on to neighboring particles, e.g., hydrogen in the case of a CO-H<sub>2</sub> mixture, or olefin in the case of olefin-CO-H<sub>2</sub>. Hence, those factors that favor methane formation in synthesis from CO and H<sub>2</sub> should be favorable to the occurrence of the hydropolymerization of olefins under the action of small amounts of CO and the hydrocondensation of CO with olefins.

Under these conditions methylene radicals do not associate, but are preserved as centers and initiators of reactions with the participation of olefins. This explains the intensity of these reactions at the stage of the "methane reaction" over a Co catalyst.

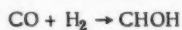
Table 3 shows that the following relation holds in Experiments 4, 5, and 8:

$$1 > (H_2/CO)_c > 2$$

This shows that not all of the CO entering the reaction of the formation of hydrocarbons is converted into methylene radicals by the equation



Part of it is evidently converted into hydroxymethylene radicals [8]



which, reacting with ethylene, give oxygen compounds. Such compounds, in particular propyl alcohol, were previously [10] found and identified in products formed in C<sub>2</sub>H<sub>4</sub>-CO-H<sub>2</sub> mixtures in presence of a Co-ThO<sub>2</sub>-kieselguhr catalyst.

## SUMMARY

1. A catalyst consisting of Co-ThO<sub>2</sub>-clay was prepared that is active in reactions leading to the formation of liquid hydrocarbons from CO-H<sub>2</sub> and CO-H<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> mixtures, and on this catalyst mutual transitions were effected of the hydrocondensation of CO with ethylene and the hydropolymerization of the latter under the action of small amounts of CO.

2. A relation was found between the molar proportions CO : H<sub>2</sub> : C<sub>2</sub>H<sub>4</sub> in the original mixture and the same proportions of these gases used in the formation of liquid hydrocarbons.

3. A theoretical explanation was given for some of the observed factors that indicate the radical-chain character of the heterogeneous catalytic hydropolymerization of ethylene under the action of small amounts of CO in presence of H<sub>2</sub>.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# COMPOSITION OF PRODUCTS OF THE BROMINATION OF 2-THIENYL KETONES IN PRESENCE OF EXCESS OF ALUMINUM CHLORIDE

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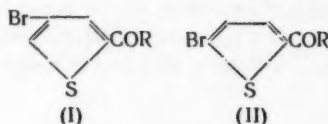
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In 1959 Gol'dfarb and one of us [1] reported that in the bromination of methyl 2-thienyl ketone in presence of 2.5 molecular proportions of anhydrous aluminum chloride the bromine enters the 4-position of the thiophene nucleus with formation of 4-bromo-2-thienylmethyl ketone (Ia) as main product. Later, the same authors [2] showed that under similar conditions the higher alkyl 2-thienyl ketones are also brominated in the nucleus with formation of 4-bromo-2-thienyl ketones (I b-e)



a —  $\text{R} = \text{CH}_3$ ; b —  $\text{R} = \text{CH}_2\text{CH}_3$ ; c —  $\text{R} = \text{CH}_2\text{CH}_2\text{CH}_3$ ; d —  $\text{R} = \text{CH}(\text{CH}_3)_2$ ;  
 e —  $\text{R} = \text{CH}_2\text{CH}(\text{CH}_3)_2$ .

In all these cases the structure of the 4-bromo-2-thienyl ketones was confirmed only by their chemical reactions (mainly oxidation to 4-bromo-2-thiophenecarboxylic acid). 5-Bromo-2-thienyl ketones were not detected in the bromination products. However, the results obtained did not yet permit us to reach conclusions concerning the purity of the 4-bromo-2-thienyl ketones and to recommend this method for preparative purposes. For the final solution of this question, 4-bromo-2-thienylmethyl ketone and some of the higher 4-bromo-2-thienyl ketones in presence of excess of aluminum chloride were subjected, without further purification, to spectrum and polarographic analysis.

The standard substances necessary for comparison were synthesized by the following methods: 4-bromo-2-thienylmethyl ketone by the debromination of 4,5-dibromo-2-thienylmethyl ketone [3]; 5-bromo-2-thienylmethyl ketone by the acylation of 2-bromothiophene in presence of stannic chloride; 4,5-dibromo-2-thienyl methyl ketone by the direct bromination of methyl 2-thienyl ketone in presence of excess of aluminum chloride. The proposed method of synthesis permits the preparation of 4,5-dibromo-2-thienyl methyl ketone in one stage in about 80% yield, which is considerably simpler and more convenient than its synthesis in four stages from the same methyl 2-thienyl ketone [4].

**Ultraviolet spectra.** The absorption spectra of the standard 4-bromo-2-thienyl methyl ketone and of the products of the bromination of 2-thienyl ketones were found to be almost identical. As would be expected, the spectra of the corresponding 5-bromo-2-thienyl ketones, taken for comparison, were also similar among themselves, but differed considerably from the spectra of 4-bromo-2-thienyl ketones in the value of the extinction coefficient of the long-wave maximum. This is undoubtedly a consequence of the presence of a substituent in the 5-position of the nucleus. The absorption curve for 5-bromo-2-thienyl methyl ketone coincided with the curve given by Pappalardo [5].



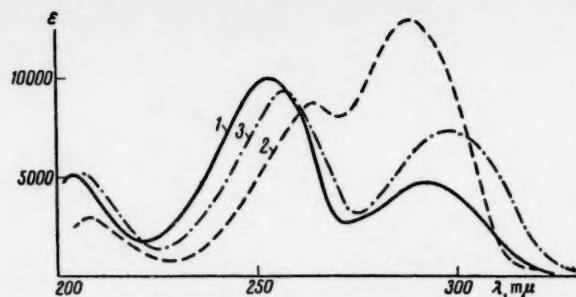


Fig. 1. Ultraviolet spectra in heptane: 1) 4-bromo-2-thienylmethyl ketone; 2) 5-bromo-2-thienyl methyl ketone; 3) 4-bromo-5-ethyl-2-thienyl methyl ketone.

Since the maxima of the absorption bands practically coincide for 4-bromo-2-thienyl ketones ( $\lambda$  292  $m\mu$ ;  $\epsilon$  4600-5000) and for 5-bromo-2-thienyl ketones ( $\lambda$  288  $m\mu$ ;  $\epsilon$  12,600-13,000) (Fig. 1), it is almost impossible to resolve the question of the purity of the bromo ketones by a comparison of ultraviolet absorption spectra. A study of artificial mixtures of (Ia) and (IIa) by this method showed that the presence of the latter can be detected with sufficient certainty by ultraviolet spectrometry only when its content in the mixture is not less than 8-10%.

For some unexplained reason, our absorption spectrum for 4-bromo-5-ethyl-2-thienyl methyl ketone differs from the spectra of 4-bromo-2-thienyl ketones not substituted in the 5-position; this is in accord with observations previously made in our laboratories concerning the difference between the absorption curves of 5-ethyl-2-thienyl methyl ketone and methyl 2-thienyl ketone.

The determination of the contents of components in mixtures by the method of infrared spectrometry has high selectivity with perfectly satisfactory accuracy. In view of the undoubted advantages of this method, we tried to apply it for the determination of the content of 5-bromo isomer in mixtures of 4- and 5-bromo-2-thienyl methyl ketones. We prepared and investigated the infrared spectra of carbon tetrachloride solutions of standard 4- and 5-bromo-2-thienyl methyl ketones in the range 700-2000  $cm^{-1}$  (Fig. 2). The spectra of these compounds differ considerably from one another. For analysis we selected the band at 990  $cm^{-1}$  belonging to 5-bromo-2-thienyl methyl ketone and the band at 1192  $cm^{-1}$  characteristic for 4-bromo-2-thienyl methyl ketone. These bands most closely meet the requirements for analytical lines. Both bands are very intense ( $\epsilon_{ef}$   $8.6 \cdot 10^3$  for 990  $cm^{-1}$  and  $\epsilon_{ef}$   $5.94 \cdot 10^3$  for 1192  $cm^{-1}$ ); also, in the region of the analytical band of one compound the other has no intense absorption bands. Checks on the sensitivity of the method showed that the presence of the 5-bromo isomer in admixture with 4-bromo-2-thienyl methyl ketone is detected with complete certainty when the content of the former is about 5% (Fig. 3).

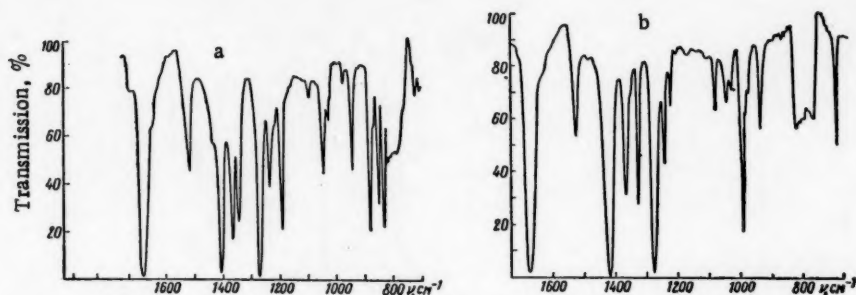


Fig. 2. Infrared spectra: a) 4- and b) 5-bromo-2-thienyl methyl ketone.

Spectroscopic investigation of the product of the bromination of methyl 2-thienyl ketone in presence of excess of aluminum chloride showed that it was 4-bromo-2-thienyl methyl ketone containing about 0.5% of the 5-bromo isomer and not more than 1% of 4,5-dibromo-2-thienyl methyl ketone, a by-product in the bromination. The spectrum that we obtained for 4,5-dibromo-2-thienyl methyl ketone showed the absence of any absorption bands of appreciable intensity in the region selected for quantitative estimation.



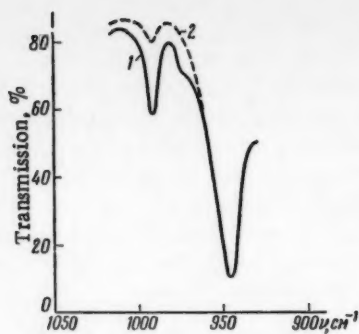


Fig. 3. Infrared spectra of mixtures of 4- and 5-bromo-2-thienyl methyl ketones in the region of the analytical band: 1) mixture containing 5% of 5-bromo-2-thienyl methyl ketone; 2) mixture containing 0.5% of 5-bromo-2-thienyl methyl ketone.

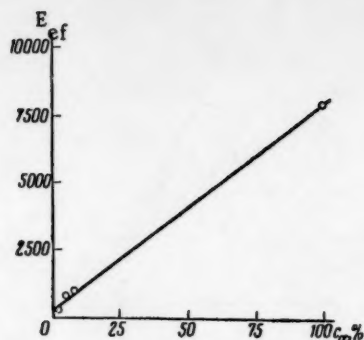


Fig. 4. Relation of the effective absorption coefficient of the band at  $990\text{ cm}^{-1}$  to the content of the 5-isomer in the mixture.

siderably more: about 15% for a content of 5-bromo-2-thienyl methyl ketone of about 10%, and 30% when its contents in the mixture was about 1%.

As the bands at  $990$  and  $1192\text{ cm}^{-1}$  probably arise from the vibrations of the thiophene ring itself, it would be interesting to determine whether they are present in the spectra of other 4- and 5-bromo-2-thienyl ketones. To verify this we determined the infrared spectra of 4- and 5-bromo-2-thienyl ethyl ketones (Fig. 5). In the spectrum of 5-bromo-2-thienyl ethyl ketone there is an intense band at  $987\text{ cm}^{-1}$ , i.e., the band is displaced by only  $3\text{ cm}^{-1}$  with respect to the spectrum of 5-bromo-2-thienyl methyl ketone, which is only slightly in excess of the error of measurement. In the spectrum of 4-bromo-2-thienyl ethyl ketone the analytical band at  $1192\text{ cm}^{-1}$  was displaced by about the same amount. Hence, it is probably possible to use this pair of analytical bands for the analysis of various 4- and 5-bromo-2-thienyl ketones.

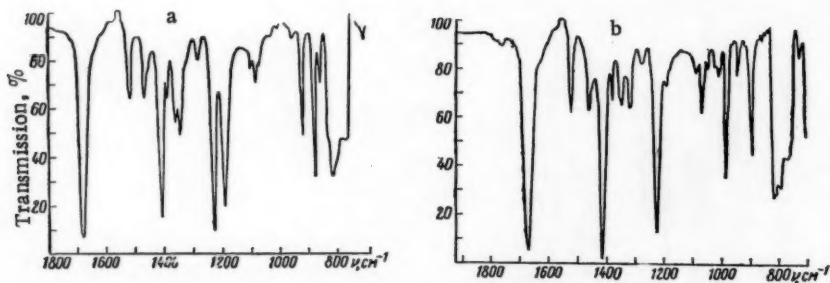


Fig. 5. Infrared spectra of a) 4- and b) 5-bromo-2-thienyl ethyl ketones.

4- and 5-Bromo-2-thienyl methyl ketones and their mixtures were subjected also to polarographic investigation, as a result of which it was shown that, after two vacuum distillations, the product of the bromination of methyl 2-thienyl ketone in presence of excess of aluminum chloride contains about 0.4% of 5-bromo-2-thienyl methyl ketone. A more detailed account of the results of the polarographic study of 4- and 5-bromo-2-thienyl methyl ketones, the accompanying bromination product, 4,5-dibromo-2-thienyl methyl ketone, and the original 2-thienyl methyl ketone will be given in a separate paper.

On the basis of our investigations we consider it possible to recommend the method of bromination of methyl 2-thienyl ketone and higher alkyl 2-thienyl ketones in presence of aluminum chloride for the synthesis of 4-bromo-2-thienyl ketones and 4,5-dibromo-2-thienyl methyl ketone, and the methods of infrared spectrometry and polarography for the quantitative analysis of mixtures of isomeric 4- and 5-bromo-2-thienyl ketones.

The polarographic investigations were carried out by S. G. Mairanovskii, to whom the authors express their thanks.

#### EXPERIMENTAL

The constants of the 4-bromo-2-thienyl ketones obtained by the bromination of the corresponding 2-thienyl ketones, and also the constants of 5-bromo-2-thienyl ketones corresponded with those cited by Gol'dfarb and one of us [2].

4-Bromo-2-thienyl methyl ketone [3] (yield 33.5%) had the following constants after two vacuum distillations: b.p. 118-120° (7 mm);  $n_D^{20}$  1.6062; semicarbazone, m.p. 212.5-213° (from alcohol). The literature [3] gives: b.p. 90-100 (1mm)  $n_D^{24}$  1.5982; semicarbazone, m.p. 210-212°.

4,5-Dibromo-2-thienyl methyl ketone. Dropwise addition was made of 3.2 g (0.025 mole) of methyl 2-thienyl ketone to 10 g (0.075 mole) of anhydrous aluminum chloride with stirring over a period of ten minutes. Rapid dropwise addition (over 2-3 minutes) was then made of 2.7 ml (0.052 mole) of bromine to the liquid complex at 40-50° (when the bromine is added more slowly, the mass solidifies before the end of the addition). The thick mass was stirred for one hour and then transferred to a mixture of ice and 10 ml of concentrated hydrochloric acid. The precipitate formed was filtered off and washed twice with water. The weight of dried 4,5-dibromo-2-thienyl methyl ketone was 5.8 g (81%). After three crystallizations from alcohol the product melted at 84-85°. The literature [4] gives m.p. 85-86°.

#### SUMMARY

1. With the aid of infrared and ultraviolet spectrometry and polarography an investigation was carried out on 4- and 5-bromo-2-thienyl methyl ketones, their mixtures, and some higher 4- and 5-bromo-2-thienyl ketones.

2. It was shown to be possible to apply infrared spectrometry and polarography for the quantitative analysis of mixtures of 4- and 5-bromo-2-thienyl methyl ketones containing from 0.5% of the latter. The method of ultraviolet spectrometry is not applicable to the quantitative analysis of mixtures of isomeric bromo-2-thienyl ketones.

3. The bromination of methyl 2-thienyl ketone and higher alkyl 2-thienyl ketones in presence of excess of aluminum chloride can serve as a preparative method of synthesizing 4-bromo-2-thienyl ketones and 4,5-dibromo-2-thienyl methyl ketone.

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## BRIEF COMMUNICATIONS

### AN IMPROVED METHOD OF DETERMINING SURFACE AREA BY THE ADSORPTION OF AIR

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In spite of the fact that numerous methods are already used in laboratory practice for determining specific surface, the search for new methods continues. This search is carried out mainly in the direction of simplifying and accelerating the method of measurement. In investigation [1], a method of the utmost simplicity for determining a surface area by the adsorption of air at the temperature of liquid oxygen is proposed. Changes which we have introduced in the construction of the apparatus and the method of measurement permit the liquid oxygen to be replaced by liquid nitrogen. Moreover, it is now possible to measure several points on the adsorption isotherm and to calculate the specific surface by the method of Brunauer, Emmett, and Teller (BET).

#### EXPERIMENTAL PART

The apparatus for the determination of a specific surface (Fig. 1) consists of a mercury manometer 1 with a scale the length of which is more than 80 cm. One tube of the manometer is sealed under vacuum and a bulb 2 with a weighed sample of the material is connected to the other through a ground joint. The tube between the ground joint and the bulb is enclosed in a vacuum jacket 3 which allows a constant cooled volume to be maintained when the bulb is immersed in liquid nitrogen. The tube connecting the bulb to the manometer possesses a branch with a three-way cock 4. The second tube of the cock communicates with the atmosphere and the third is connected through a ground joint with a bulb 5 containing a few grams of active carbon.

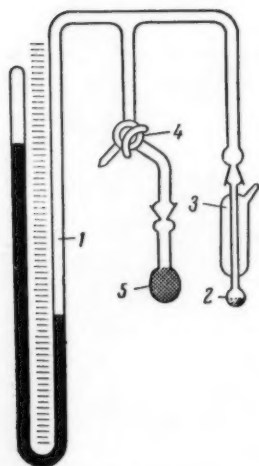


Fig. 1. Plan of the apparatus.

To determine a specific surface, a weighed sample is placed in the bulb and this is connected to the apparatus. The bulb containing carbon is connected to the manometer and immersed in liquid nitrogen. After all the air in the apparatus has been adsorbed on the carbon, the liquid nitrogen is removed and desorption of the gases begins. When the pressure in the manometer reaches 100-250 mm, the bulb containing charcoal is cut off from the manometer and connected with the atmosphere by turning the cock. The pressure of gas in the manometer is measured on the scale with an accuracy of  $\pm 0.5$  mm and recorded. The tube with the sample is immersed in liquid nitrogen and the new pressure established is recorded after some minutes. The adsorption may be determined from the measurement of the pressure on cooling the sample. Let us introduce the following symbols:  $P_0$  and  $P_1$  are the manometer readings before and after adsorption on the sample;  $V_1$  is the volume of the cooled tube;  $V_2$  is the volume of the rest of the apparatus at  $p = 0$ ;  $T_K$  and  $T_a$  are room temperature and the temperature of liquid nitrogen;  $r$  is the radius of the manometer tube; and  $m$  is the weight of the sample. The adsorption is determined from the formula:

$$\begin{aligned} a &= \frac{1}{RT_K} (V_1 + V_2 + \frac{\pi r^2}{2} p_0) p_0 - \frac{1}{RT_K} (V_2 + \frac{\pi r^2}{2} p_1) p_1 \frac{V_1 p_1}{RT_a} = \\ &= \frac{1}{RT_K} \left\{ (p_0 - p_1) \left[ V_1 + V_2 + \frac{\pi r^2}{2} (p_0 + p_1) \right] - V_1 p_1 \left( \frac{T_K}{T_a} - 1 \right) \right\}. \end{aligned}$$

If the pressure is expressed in mm Hg and the volume in  $\text{cm}^3$ , the adsorption in  $\mu\text{m/g}$  is:

$$a = \frac{16,04}{mT_K} \left\{ (p_0 - p_1) \left[ V_1 + V_2 + \frac{\pi r^2}{2} (p_0 + p_1) \right] - V_1 p_1 \left( \frac{T_K}{T_1} - 1 \right) \right\}.$$

If the weight of the sample is high, then its volume, equal to  $m/d$ , where  $d$  is the true density of the sample, must be deducted from the volume  $V_1$ .

When the apparatus is first used, the volumes appearing in the equation must be measured. The radius of the manometer tube and the volume of the cooled part of the bulb can easily be directly measured by calibration with mercury. If the two arms of the manometer have different radii, the magnitude  $\frac{\pi r_1^2 r_2^2}{r_1^2 + r_2^2}$  is used in the equation

instead of  $\frac{\pi r^2}{2}$ . The volume  $V_2$  may be determined in the following way. The change in pressure on cooling the

empty bulb at various initial pressures is measured. Taking  $a = 0$ , we obtain an equation where all the magnitudes except  $V_2$  are known. This calibration must be carried out each time a new bulb is brought into use. The constants of the apparatus may be checked by measuring the adsorption on samples with an accurately known surface.

The sensitivity of the method depends on the geometrical dimensions of the apparatus. In our apparatus  $\pi r^2/2 = 0.098 \text{ cm}^2$ ,  $V_1 = 2.5 \text{ cm}^3$ , and  $V_2 = 23.3 \text{ cm}^3$ . With these dimensions, good results are obtained in those cases when the surface of the sample is  $7\text{--}15 \text{ m}^2$ . The sample must be chosen in such a way that a total surface close to this value is obtained. Thus, for materials with a surface of  $100 \text{ m}^2/\text{g}$ , a sample of  $\sim 0.1 \text{ g}$  is required. If, on carrying out the measurements, it is found that the surface of the sample differs considerably from the value given, it is desirable to repeat the measurements with another sample. Decreasing the volume of the apparatus may increase its sensitivity (but not its accuracy).

The specific surface is determined from the formula:

$$S = \alpha_m \omega_0 N,$$

where  $N$  is Avogadro's number;  $\omega_0$  is the molecular area of nitrogen,  $16.2 \text{ \AA}^2$ ; and  $\alpha_m$  is the capacity of a monolayer in  $\text{M/g}$ . To determine the capacity of a monolayer, the adsorption may be measured at several pressures and the BET method applied [2]. The approximate capacity of a monolayer is determined by a single point method [3] from the formula  $\alpha_m \approx a(1 - p/p_s)$ . This method gives good results for large values of the constant  $C$  in the BET equation.

A simple method for determining the surface from a single adsorption point can be proposed. The change in the pressure on cooling the empty bulb rises linearly with an increase in the final pressure:  $\Delta p_0 = a_0 + b_0 p_1$ . If a sample of material is placed in the bulb, then a straight line is again obtained but it lies above, and its slope is greater than, that for the empty bulb:  $\Delta p = a + b p_1$ . The greater the surface of the sample, the greater the magni-

tudes  $a$  and  $b$ , the magnitudes  $A = \frac{a - a_0}{S}$  and  $B = \frac{b - b_0}{S}$  not depending on the surface. The surface of the sample

may be determined from the formula:  $S = \frac{\Delta p - \Delta p_0}{m(A + B p_1)}$ . To find the constants  $A$  and  $B$ , it is necessary to measure

the adsorption of several materials with a known surface or of various weights of a single material and to take the mean value. When the constants  $a_0$ ,  $b_0$ ,  $A$ , and  $B$  have been determined, it is sufficient to measure  $\Delta p$  at any final pressure  $p_1$  in order to determine the surface. This empirical method permits a very rapid measurement of the specific surface from a single point with an error not greater than in the BET method.

To check the proposed method, the adsorption of a series of materials with a known surface was carried out. The results obtained are given in the Table. For comparison, the surfaces determined by a gravimetric method with the adsorption of benzene vapours and by a volumetric method with the adsorption of krypton are given. The

Sample	S <sub>air</sub>	S <sub>Kr</sub>	S <sub>C.H.</sub>	Error, %
Cr <sub>2</sub> O <sub>3</sub>	21,5 23,2	22		- 2,5 + 5,5
Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> (18%)	133		122	+ 9
Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> (40%)	90		76	+15
ZnO	4,4	4,04; 4,4		+ 9; 0
Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> O (№ 1)	80	85,7		- 7
Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> O (№ 2)	154	178		-13
TiO <sub>2</sub>	3,0	2,85		+ 5
Catalyst A <sub>7</sub>	84		74	+13,5
ZrO <sub>2</sub> (№ 5)	43	39		+10
MgO	77	74		+ 4
Fe-Al <sub>2</sub> O <sub>3</sub>	1,7	1,7		0
Ho <sub>2</sub> O <sub>3</sub>	38	36		+ 6
Sm <sub>2</sub> O <sub>3</sub>	15,2	15,6		- 2,5

difference in the figures for the surfaces amounts to  $\pm 10-15\%$ . This is not such a large spread if it is considered that the best methods of determining specific surfaces, which include those with which the comparison is being made, have an accuracy of not higher than  $\pm 5\%$ . If a series of similar samples are measured under identical conditions (weight of sample, temperature of liquid nitrogen), the relative error of the measurements is considerably reduced. Thus, for four similar samples of ZrO<sub>2</sub>, values of 40.5, 43, 40, and 40 m<sup>2</sup>/g were obtained.

The fact that the measurement of adsorption by the proposed simplified method is associated with some assumptions which introduce errors must not be omitted. The change in the temperature of the liquid nitrogen is not taken into account; the calculation of the surface is carried out as if for the adsorption of pure nitrogen. Oxygen is, of course, present with it in air. The surface is measured without previously pumping out the samples. In many cases this is of no importance, but for some materials a preliminary heating of the samples to remove adsorbed water is necessary.

In spite of the drawbacks present, the method of determining the surface from the adsorption of air gives satisfactory results in a wide range of magnitudes of the surface; it may find wide application in view of its simplicity. To determine a surface by the single-point method requires not more than 15 min. Even when more accurate methods are available, the rapid evaluation of a surface is very useful since it makes it possible to choose the weight of the sample correctly. The method may be used with success in the case where the measurement of the surface of a large number of similar samples is required.

#### SUMMARY

A simple method has been proposed for the rapid approximate determination of specific surfaces by the adsorption of air at a low temperature.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.



# THE SYNTHESIS OF ALKENYLSILANES BY THE HIGH-TEMPERATURE CONDENSATION OF UNSATURATED COMPOUNDS WITH SILICON HYDRIDES

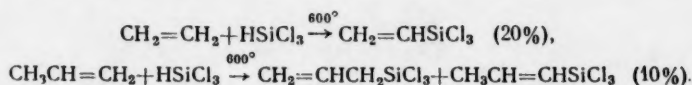
V. F. Mironov and V. V. Nepomnina

The N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR

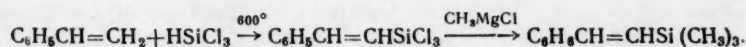
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, pp. 1886-1888, October 1961

Original article submitted April 3, 1961

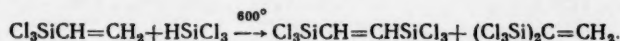
It has previously been established [1-3] that ethylene and propylene form the corresponding alkenylsilanes on being heated for a short time with silicon hydrides to  $\sim 600^\circ$



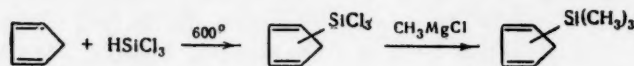
In developing this reaction, new in the organic chemistry of silicon, we have investigated the high-temperature condensation of trichlorosilane with styrene, cyclopentadiene, and vinyltrichlorosilane. Styrene undergoes high-temperature condensation with trichlorosilane, giving a 15% yield of  $\beta$ -trichlorosilylstyrene, the structure of which was shown by its methylation and the complete agreement of the properties and IR spectra of the substance obtained with those of known  $\beta$ -trimethylsilylstyrene



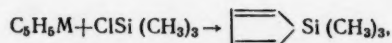
The condensation of trichlorosilane with vinyltrichlorosilane gave a 10% yield of a mixture of disilyl-substituted ethylenes



Consequently, the still residue in the synthesis of vinyltrichlorosilane from vinyl chloride and  $\text{HSiCl}_3$  by the high-temperature condensation method [2-5] must contain the above mentioned compound. And, finally, the high-temperature condensation of cyclopentadiene (or its dimer) with trichlorosilane gave a 25% yield of cyclopentadienyltrichlorosilane



The properties of the cyclopentadienyltrimethylsilane which we obtained did not agree with the properties of the compound obtained earlier [6,7] by the organometallic route



where  $\text{M} = \text{Li}, \text{MgBr}$ .

This cyclopentadienyltrimethylsilane, which was assigned the structure given without proof, reacts vigorously in ether with maleic anhydride and forms an adduct with m.p.  $102^\circ$ . Our compound does not react with maleic anhydride under these conditions. The Raman and infrared spectra of the two cyclopentadienylsilanes also differ fundamentally (Figs. 1 and 2).

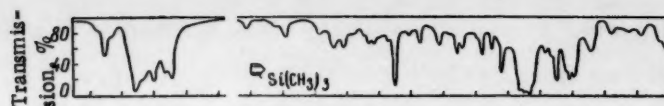


Fig. 1

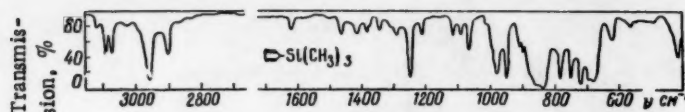
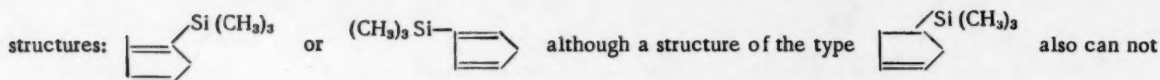


Fig. 2

From these facts it may be assumed that the cyclopentadienylsilane obtained by us has one of the following



be rejected at present.

## EXPERIMENTAL

**Cyclopentadienyltrichlorosilane  $C_5H_5SiCl_3$ .** A mixture consisting of 133 g of cyclopentadiene dimer (cyclopentadiene may be used) and 338 g of trichlorosilane was passed through an empty quartz tube (100 mm long and 15 mm in diameter) heated to  $600 \pm 10^\circ$  at a rate of 2 drops per sec. ( $\sim 4$  g/hr). Distillation of the condensate yielded 44 g of cyclopentadienyltrichlorosilane with m.p.  $72^\circ$  (30 mm);  $n_D^{20}$  1.4972;  $d_4^{20}$  1.2338; Found MR 47.30; Calculated MR 44.62; yield, 24.8%. Found: Cl, 54%.  $C_5H_5SiCl_3$ . Calculated: Cl, 53.3%.

**Cyclopentadienyltrimethylsilane  $C_5H_5Si(CH_3)_3$ .** To the  $CH_3MgCl$  obtained from 28 g of magnesium in 0.8 l of ether, 40 g of  $C_5H_5SiCl_3$  was added. The contents of the flask were boiled for 4 hours and were treated with water. The ethereal layer and ethereal extracts of the aqueous layer were combined and dried with  $CaCl_2$ . Distillation in a column yielded 16 g of  $C_5H_5Si(CH_3)_3$  with b.p.  $138-140^\circ$ ;  $n_D^{20}$  1.4610;  $d_4^{20}$  0.8334; found MR 45.45; calculated MR 45.75; yield 59%. Found: Si, 20.20; 20.53%.  $C_5H_{14}Si$ . Calculated: Si, 20.31%.

Raman spectrum ( $\Delta\nu$ ,  $cm^{-1}$ ). 151 (5), 219 (10b), 418 (3), 580 (6b), 625 (8b), 644 (1), 674 (5), 733 (1), 909 (2), 980 (0), 1005 (2), 1032 (2), 1110 (10), 1126 (1), 1176 (4), 1208 (0), 1255 (1), 1386 (3), 1412 (2), 1444 (2), 1464 (1), 1579 (0), 1609 (8), 1648 (5), 1698 (0), 2905 (10b), 2965 (10b).

Literature data [9]: b.p.  $96-97^\circ$  (12 mm);  $n_D^{20}$  1.5214;  $d_4^{20}$  0.8886; MR 60.45. The Raman spectrum of this substance agreed completely with the previously published spectrum for  $C_6H_5CH=Si(CH_3)_3$  [9].

The cyclopentadienyltrimethylsilane obtained by us by Frisch's method [7] had b.p.  $140^\circ$  (747 mm);  $n_D^{20}$  1.4627;  $d_4^{20}$  0.8326; found MR 45.71; calculated MR 45.73.

Raman spectrum ( $\Delta\nu$ ,  $cm^{-1}$ ) 151 (2), 198 (1), 217 (5b), 256 (1), 278 (1), 309 (0), 404 (1), 420 (9), 597 (0), 618 (10), 633 (3), 676 (1), 697 (2), 725 (2), 758 (1b), 785 (1), 821 (1), 837 (1b), 867 (3), 911 (2), 955 (4), 980 (8vb), 997 (0), 1017 (2), 1092 (3b), 1116 (4), 1192 (1), 1222 (0), 1260 (2b), 1309 (0), 1348 (1), 1386 (3sh), 1463 (10), 1485 (7sh), 2882 (1), 2905 (8b), 1964 (7b), 3076 (7).

**$\beta$ -(Trichlorosilyl)-styrene  $C_6H_5CH=CHSiCl_3$ .** A mixture consisting of 104 g of styrene and 148 g of trichlorosilane was passed through the above-mentioned tube during 3 hours at  $600^\circ$ . Distillation in a column yielded 31.5 g of  $C_6H_5CH=CHSiCl_3$  with b.p.  $90-93^\circ$  (2 mm);  $n_D^{20}$  1.5540;  $d_4^{20}$  1.2718; found MR 59.87; calculated [8] MR 59.95; yield 15%. Found: Cl 44.50%.  $C_6H_7SiCl_3$ . Calculated: Cl 44.76%. Literature data [9]: b.p.  $133^\circ$  (10 mm);  $n_D^{20}$  1.5575;  $d_4^{20}$  1.2848; MR 59.58.

**$\beta$ -(Trimethylsilyl)-styrene  $C_6H_5CH=CHSi(CH_3)_3$ .** To the  $CH_3MgCl$  obtained from 23 g of magnesium in 0.5 l of ether, 31 g of  $C_6H_5CH=CHSiCl_3$  was added. After the usual working up, vacuum distillation yielded 20 g of  $C_6H_5CH=CHSi(CH_3)_3$  with b.p.  $75-77^\circ$  (5 mm);  $n_D^{20}$  1.5206;  $d_4^{20}$  0.8910; found MR 60.22; calculated [8] MR 60.41. Literature data [9]: b.p.  $96-97^\circ$  (12mm);  $n_D^{20}$  1.5214;  $d_4^{20}$  0.8886; MR 60.45. The Raman spectrum of this substance agreed completely with the previously published spectrum for  $C_6H_5CH=Si(CH_3)_3$  [9].

1,1- and 1,2-(Trichlorosilyl)-ethylenes  $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$  and  $(\text{Cl}_3\text{Si})_2\text{C}=\text{CH}_2$ . A mixture consisting of 81 g of vinyltrichlorosilane and 81 g of trichlorosilane was passed through the above-mentioned tube during 4 hours at  $600^\circ$ . Distillation in a column yielded 26 g of  $\text{HSiCl}_3$  with b.p.  $31-32^\circ$ ; 52 g of  $\text{SiCl}_4$  with b.p.  $56^\circ$ ; 10 g of  $\text{Cl}_3\text{SiCH}=\text{CH}_2$  with b.p.  $92^\circ$ , and 14 g of a fraction with b.p.  $197-200^\circ$ , yield 10.2%. Analysis of the Raman spectrum of this fraction showed that it consisted of  $\text{Cl}_3\text{SiCH}=\text{CHSiCl}_3$ ,  $(\text{Cl}_3\text{Si})_2\text{C}=\text{CH}_2$ , and aromatic compounds.

The Raman spectrum were taken and analyzed by L. A. Leites, to whom we express our deep thanks.

#### SUMMARY

The general character of the new high-temperature reaction of unsaturated hydrocarbons with silicon hydrides, leading to the formation of unsaturated organosilicon compounds, has been shown on the basis of new examples.

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#### THE $\beta$ -ALLYLOXYETHYL n-BUTYL ACETAL OF ACETALDEHYDE

A. K. Gorban'

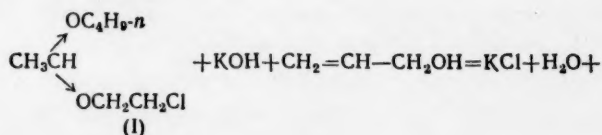
The N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR

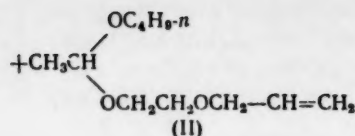
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 10, pp. 1889-1890, October 1961

Original article submitted March 31, 1961

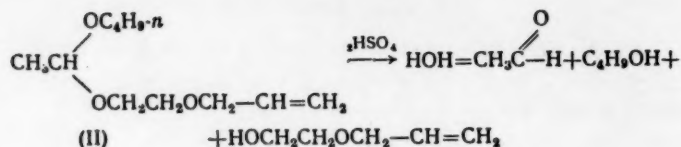
In investigating the replacement of chlorine in  $\beta$ -chloroethyl alkyl acetals [1] by the ethoxy group, we proposed a method of synthesis of alkyl  $\beta$ -ethoxyethyl acetals by the reaction of an ethanolic solution of caustic potash and  $\beta$ -chloroethyl alkyl acetals. We showed that when ethyl  $\beta$ -chloroethyl acetal and n-butyl  $\beta$ -chloroethyl acetal were boiled with a solution of caustic potash in ethanol, the corresponding ethyl  $\beta$ -ethoxyethyl and n-butyl  $\beta$ -ethoxyethyl acetals were formed [2].

The present investigation was undertaken with the aim of replacing the chlorine of  $\beta$ -chloroethyl alkyl acetals by an unsaturated alkoxy group. As has been shown, when the ethanol is replaced by allyl alcohol,  $\beta$ -chloroethyl butyl acetal forms, under similar conditions, the corresponding  $\beta$ -allyloxyethyl n-butyl acetal of acetaldehyde (II) in the form of a colorless mobile liquid insoluble in water.





Acetals with the unsaturated allyloxy group in the  $\beta$ -position possess not only theoretical interest but also practical interest for the production of copolymers. The structure of the  $\beta$ -allyloxyethyl n-butyl acetal of acetaldehyde obtained (II) was demonstrated by its hydrolysis with 2% sulfuric acid. Allyloxyethanol, butanol, and acetaldehyde were formed, the latter being determined quantitatively by the bisulfite method [1-3].



The  $\beta$ -allyloxyethyl n-butyl acetal of acetaldehyde (II) has been obtained previously by the interaction of vinyl n-butyl ether and allyloxyethanol [4].

## EXPERIMENTAL

**Production of the  $\beta$ -allyloxyethyl n-butyl acetal of acetaldehyde (II).** A mixture of 10 g (0.178 mole) of caustic potash and 15 g (0.258 mole) of allyl alcohol was placed in a three-necked flask fitted with a mercury seal, a reflux condenser, a mechanical stirrer, a thermometer, and a dropping funnel. The solution was heated to boiling and then 22 g (0.122 mole) of n-butyl  $\beta$ -chloroethyl acetal (I) was added over 10 min.

After boiling for several hours, the reaction mixture, in contrast to previous experiments [2], was washed with water and the substance separating was dried with potash and distilled in vacuum. In this way, 2.5 g (10% of theory) of the  $\beta$ -allyloxyethyl n-butyl acetal of acetaldehyde (II) was obtained, with b.p. 86.5-87° (5 mm);  $d_4^{20}$  0.9081;  $n_D^{20}$  1.4290. Found: C, 65.10, 64.90; H, 10.90, 10.70%; MR 57.40. Calculated: C, 65.30; H, 10.96%; MR 57.90.

**Hydrolysis of the  $\beta$ -allyloxyethyl n-butyl acetal of acetaldehyde (II).** A sample (0.1-0.2 g) of the  $\beta$ -allyloxyethyl n-butyl acetal (II) in a small thin-walled bulb was placed in a 300 ml conical flask with a ground stopper together with 20 ml of 2% sulfuric acid and 20 ml of a 0.2 N solution of sodium bisulfite. The bulb was broken by shaking, and the reaction mixture was allowed to stand at room temperature for not more than half an hour and was then titrated with 0.1 N iodine solution in the presence of starch. The amount of acetal found was 97.4, 101.9%.

## SUMMARY

The  $\beta$ -allyloxyethyl n-butyl acetal of acetaldehyde has been obtained by the reaction of the solution of caustic potash in allyl alcohol with  $\beta$ -chloroethyl n-butyl acetal, and characterized.

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# THE REACTION OF POLY-(VINYL ALCOHOL) WITH POLY-(METHACRYLIC ACID)

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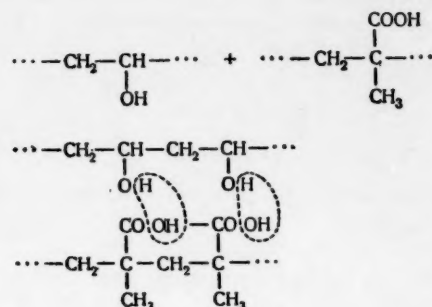
Original article submitted April 3, 1961

The high reactivity of poly-(vinyl alcohol), which contains secondary alcohol groups, is shown in numerous reactions. It is known that the hydroxyl groups of poly-(vinyl alcohol) react with acids and aldehydes [1] and also add readily to the double bond of vinyl ethers with the formation of acetals [2]. The activity of the hydroxyl groups of poly-(vinyl alcohol) is so high that the formation of acetals with vinyl ethers is found even when these compounds react in an aqueous medium [3]. However, the activity of the hydroxyl groups of poly-(vinyl alcohol) has not been studied at all with respect to their reaction with polymers containing functional groups with labile hydrogen, for example with polymers of acids of the acrylic series.

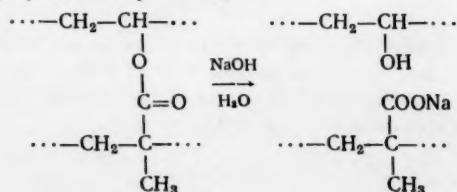
In order to investigate this question, experiments have been carried out on the interaction of aqueous solutions of poly-(vinyl alcohol) and poly-(methacrylic acid) at room temperature without the use of catalysts. The reaction was carried out with equimolecular ratios of the starting materials (calculated with respect to a link of the chain) or with an excess of one of them.

In all cases, the esterification reaction proceeded almost quantitatively; the beginning of the reaction was very clear, since the highly water-soluble poly-(vinyl alcohol) and poly-(methacrylic acid), on reaction, gave new substances which were insoluble in water and readily separated out from aqueous solution.

The scheme of the reaction is as follows



The new polyesters formed may belong to the type of the so-called cross-linked high-molecular-weight compounds. In fact, the polyesters obtained are insoluble in water and organic solvents and carbonize in heating, without melting. In order to establish the structure of these polyesters, they were subjected to alkaline hydrolysis. The polyesters were completely hydrolysed in an aqueous solution of caustic soda with the formation of poly-(vinyl alcohol) and the sodium salt of poly-(methacrylic acid)





Initial substance	Molar ratio	Yield, % of theory	Content of poly-(methacrylic acid) links		Amount of poly-(methacrylic acid) which has not reacted, %
			Theoretical, %	Actual, %	
Poly-(vinyl alcohol)	1	99.0	61.6	59.0	1.07
Poly-(methacrylic acid)	1				
Poly-(vinyl alcohol)	0.5	91.6	61.6	58.6	41.6
Poly-(methacrylic acid)	1				
Poly-(vinyl alcohol)	1	94.5	61.6	59.4	0.97
Poly-(methacrylic acid)	0.5				

A corresponding experiment using an aqueous solution of poly-(vinyl alcohol) was carried out to study the reaction between poly-(vinyl alcohol) and monomeric methacrylic acid; in this case, the reaction took place considerably more slowly. Thus, it has been established that the esterification reaction of the given polymers takes place in aqueous solution almost quantitatively.

#### EXPERIMENTAL

The following were used as starting materials for the synthesis of the polyester of vinyl alcohol and methacrylic acid: poly-(vinyl alcohol) containing 1.5% of acetate groups, sp. gr. 1.259, and methacrylic acid having b.p. 160°,  $n_D^{20}$  1.4313,  $d_4^{20}$  1.0153, acid number 650 mg of KOH.

The methacrylic acid polymer was synthesized by us. Methacrylic acid was polymerized in the presence of 0.2% of benzoyl peroxide and the polymer obtained was then precipitated from methanol with benzene. Precipitation was repeated several times until no qualitative reaction for a double bond was given. Then the poly-(methacrylic acid) was dried to constant weight and analysed. It contained 99.5% of carboxyl groups. For the synthesis of the polyester, 10% aqueous solutions of the poly-(vinyl alcohol) and poly-(methacrylic acid) were used. The aqueous solutions were mixed at room temperature; after some minutes, the solution began to become turbid and a precipitate of the polyester separated. The latter was washed with water to neutrality and dried to constant weight. The content of poly-(methacrylic acid) which had not reacted was determined in the aqueous filtrate titrimetrically. The polyester was saponified with a solution of alkali and the carboxyl groups determined by titration. Then the amount of poly-(methacrylic acid) present in the polyester was calculated. The results obtained are given in the Table.

#### SUMMARY

1. A new type of polyester of poly-(vinyl alcohol) and poly-(methacrylic acid) has been synthesized.
2. The condensation of poly-(vinyl alcohol) and poly-(methacrylic acid) takes place in an aqueous medium almost quantitatively at room temperature.

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PHASE TRANSFORMATIONS IN THE PREPARATION OF Ni-MgO  
CATALYSTS BY THE DECOMPOSITION OF OXALATES IN A  
CURRENT OF HYDROGEN

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It is known that salts of nickel and magnesium may form mixed salts. On decomposing such salts of the oxalates and formates in a current of hydrogen, highly active Ni-MgO hydrogenation catalysts are obtained [1]. Even more active catalysts are obtained on decomposing the mixed oxalates in a vacuum [2]. The phase transformations in the decomposition of the mixed salts and the composition of the catalysts formed have been inadequately studied [1,3]. In the present work, the phase transformations in the preparation of Ni-MgO catalysts from mixed oxalates have been investigated by the X-ray method. The nickel and magnesium oxalates and the mixed oxalates were obtained by the procedure given in [1].

TABLE 1. Composition of Simple and Mixed Oxalates of Nickel and Magnesium

Sample No.	Composition, % by weight				Content of nickel and magnesium oxalates, moles %	
	Ni	Mg	C <sub>2</sub> O <sub>4</sub>	H <sub>2</sub> O	Ni	Mg
1	32,6	—	45,6	21,8	100	—
2	26,1	1,3	49,3	23,3	89	11
3	18,5	5,0	52,7	23,8	60	40
4	16,3	7,0	54,7	22,0	49	51
5	12,4	9,2	55,0	23,4	36	64
6	—	17,0	59,0	24,0	—	100

TABLE 2. Conditions of the Decomposition of the Oxalates in a Current of Hydrogen and Results of the Phase Analysis of the Solid Products Obtained

Sample No.	Temperature, °C	Time, hr.	Crystalline phases observed
1	200	1	β -Ni
	350	1	β -Ni
2	200	0.5	Anhydrous (Ni, Mg) C <sub>2</sub> O <sub>4</sub>
	350	1	β -Ni, MgO
	350	11	β -Ni, MgO
	450	1	β -Ni, MgO
6	200	1	Anhydrous MgC <sub>2</sub> O <sub>4</sub>
	350	1	Anhydrous MgC <sub>2</sub> O <sub>4</sub>
	450	2	Anhydrous MgC <sub>2</sub> O <sub>4</sub> , MgO
	450	6	MgO

The composition of these oxalates determined by permanganate titration of the oxalate ions, precipitation of the nickel by dimethylglyoxime, and combustion are given in Table 1. On calcining the oxalates obtained in air

TABLE 3. Interplanar Spacings and Relative Intensities\* of the Lines for the Hydrated Oxalates of Samples 1-6

Line number	1		2		3		4		5		6	
	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å
1	оя	4,7	оя	4,7	оя	4,7	оя	4,8	оо	4,8	оя	4,8
2	ср	4,0	яср	3,9	ср	3,9	ср	3,9	ср	3,9	сл	3,8
3	—	—	—	—	—	—	—	—	сл	3,4	сл	3,3
4	яср	2,94	я	2,95	яср	3,0	яср	3,1	я	3,1	я	3,2
5	оосл	2,64	оосл	2,65	—	—	—	—	—	—	—	—
6	ср	2,51	яср	2,50	ср	2,52	ср	2,53	яср	2,53	срсл	2,54
7	—	—	—	—	—	—	—	—	—	—	сл	2,47
8	оосл	2,36	осл	2,35	срсл	2,38	срсл	2,38	ср	2,38	ср	2,37
9	срсл	2,20	срсл	2,18	срсл	2,20	сл	2,20	—	—	—	—
10	ср	2,05	ср	2,05	ср	2,06	ср	2,07	яср	2,07	срсл	2,08
11	—	—	—	—	—	—	сл	2,03	яср	2,01	яср	2,03
12	ср	1,90	ср	1,91	срсл	1,95	срсл	1,96	—	—	—	—
13	ср	1,86	ср	1,84	ср	1,86	ср	1,86	яср	1,86	ср	1,86
14	сл	1,75	сл	1,75	сл	1,76	сл	1,76	срсл	1,77	осл	1,77
15	—	—	—	—	—	—	—	—	осл	1,64	—	—
16	срсл	1,58	осрсл	1,57	сл	1,58	срсл	1,59	срсл	1,60	сл	1,60
17	—	—	—	—	—	—	—	—	осл	1,57	осл	1,59
18	осл	1,51	осл	1,51	сл	1,49	срсл	1,50	ср	1,52	срсл	1,52
19	—	—	—	—	—	—	—	—	сл	1,50	оосл	1,50
20	сл	1,46	сл	1,47	оосл	1,43	оосл	1,45	оосл	1,46	оосл	1,47
21	оосл	1,41	оосл	1,40	—	—	—	—	—	—	—	—
22	оосл	1,35	оосл	1,36	оосл	1,34	осл	1,34	осл	1,34	сл	1,35
23	сл	1,31	—	—	оосл	1,31	оосл	1,32	осл	1,32	осл	1,30
24	сл	1,298	сл	1,293	осл	1,293	сл	1,293	сл	1,291	осл	1,283
25	—	—	оосл	1,264	—	—	—	—	оосл	1,272	оосл	1,272
26	—	—	—	—	—	—	—	—	оосл	1,259	оосл	1,262
27	—	—	—	—	осл	1,239	сл	1,241	сл	1,237	осл	1,242
28	осл	1,226	осл	1,229	—	—	—	—	—	—	—	—
29	—	—	—	—	—	—	—	—	осл	1,201	осл	1,203
30	осл	1,194	оосл	1,197	оосл	1,193	сл	1,193	осл	1,194	оосл	1,191
31	оосл	1,159	оосл	1,163	—	—	—	—	—	—	—	—
32	—	—	—	—	—	—	—	—	—	—	оосл	1,138
33	—	—	—	—	—	—	оосл	1,121	осл	1,120	сл	1,122
34	оосл	1,100	оосл	1,111	оосл	1,118	оосл	1,110	—	—	оосл	1,099

\*Here and in Table 4, the intensities of the lines are denoted in the following way: оо ) very very intense; оя ) very intense; я ) intense; яср ) intense-medium; ср ) medium; срсл ) medium-weak; сл ) weak; осл ) very weak; оосл ) very very weak.

at 150°, complete dehydration was achieved only the case of magnesium oxalate (sample 6); the loss in weight amounted to 23% and chemical analysis confirmed that anhydrous magnesium oxalate was obtained in this case. On calcining the other samples, the loss in weight after 80 hr. was only 1-7%. However, in vacuum ( $10^{-3}$  mm Hg) at 140-150°, practically complete dehydration of all the samples was achieved in 15-20 hr. Samples 1 (nickel oxalate), 2 (a mixed oxalate), and 6 (magnesium oxalate) were heated in a current of hydrogen at 200, 350, and 450° under conditions similar to those described by Langenbeck [1] (Table 2). The catalysts obtained by the decomposition of one of the mixed oxalates (sample 2) proved extremely active in hydrogenation, the catalyst prepared at 350° being more active than that prepared at 450°. The activity of the catalyst was determined by the absorption of hydrogen in the hydrogenation of eugenol at 20° in ethyl alcohol.

The X-ray diagrams were obtained using filtered Cu and Fe radiation (voltage 35 kV, anode current 12 mA) in a RFD camera. Pyrophoric samples were exposed in an inert filler (Canada balsam or vaseline oil). The interplanar distances and the relative intensities of the lines for the hydrated oxalates are given in Table 3 and those for the anhydrous compounds in Table 4. It can be seen from Table 3 that the X-ray diagrams of the hydrated oxalates of nickel and magnesium are extremely complex; the mixed oxalates form a single-phase system and give an intermediate X-ray picture. With a change in the concentration of the cation, a gradual transition from the picture of

TABLE 4. Interplanar Distances and Relative Intensities of the Lines for the Anhydrous Oxalates of Samples 1-6

Line number	1		2		3		4		5		6	
	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å
1	—	—	—	—	—	—	—	—	—	—	оя	5,25
2	—	—	—	—	—	—	—	—	—	—	оя	4,00
3	ооа*	3,65	ооа	3,65	ооа	3,65	ооа	3,65	ооа	3,65	сря	3,69
4	—	—	—	—	—	—	—	—	—	—	сря	3,19
5	—	—	—	—	—	—	—	—	—	—	сря	2,76
6	—	—	—	—	—	—	—	—	—	—	сря	2,58
7	—	—	—	—	—	—	—	—	—	—	я	2,44
8	оя	2,34	оя	2,34	оя	2,34	оя	2,34	оя	2,32	сря	2,31
9	сря	2,14	сря	2,14	сря	2,16	сря	2,12	ясп	2,14	сл	2,11
10	—	—	—	—	—	—	—	—	—	—	сря	1,91
11	оя	1,84	оя	1,84	сл	1,84	сл	1,82	сл	1,84	сря	1,84
12	я	1,74	сл	1,74	оя	1,74	оя	1,75	я	1,74	сря	1,75
13	—	—	—	—	—	—	—	—	—	—	оосл	1,72
14	—	—	—	—	—	—	—	—	—	—	оя	1,53
15	сл	1,45	сл	1,45	сл	1,45	сл	1,45	сл	1,45	сл	1,45
16	—	—	—	—	—	—	—	—	—	—	оосл	1,39
17	сря	1,32	сл	1,32	сря	1,33	сря	1,34	сл	1,33	сл	1,34
18	осл	1,24	осл	1,24	осл	1,25	осл	1,25	осл	1,25	сл	1,25
19	—	—	—	—	—	—	—	—	—	—	оосл	1,22

\* Designations same as in Table 3.

one oxalate to that of the other is found. Data on the interplanar spacings and relative intensities of the lines for the anhydrous oxalates has been obtained in the present work for the first time. It can be seen from a comparison of Tables 3 and 4 that the X-ray diagrams of the anhydrous oxalates of nickel and magnesium are completely different and that the mixed oxalates give the same X-ray picture as nickel oxalate. The phase compositions of the solid products of the decomposition of the oxalates under various conditions are given in Table 2. Even at 200°, nickel oxalate is reduced to metallic nickel in hydrogen. Heating magnesium oxalate in a current of hydrogen at 200° and 350° led to the formation of anhydrous magnesium oxalate. Only at 450° did the lines of MgO appear in the X-ray diagrams, and they became the only ones after 6 hours calcination. In air, according to the data of Ugai [4], nickel oxalate decomposes at 400-405° and magnesium oxalate at 419-421°. Decomposition of the mixed oxalate in a current of hydrogen at 200° yielded a sample the X-ray diagram of which was the same as for the mixed anhydrous oxalate. At 350 and 450°, samples were obtained containing two phases: metallic nickel (the cubic modification,  $\beta$ -Ni) and magnesium oxide.

#### SUMMARY

1. The formation of Ni-MgO catalysts proceed through the stage of anhydrous mixed oxalates. Only two crystalline phases are found in the active catalyst:  $\beta$ -Ni, and MgO.
2. The anhydrous simple and mixed oxalates of nickel and magnesium have been obtained and identified by X-ray means for the first time.

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# THE PRODUCTION OF DIALKYLALUMINIUM HYDRIDES FROM DIALKYLALUMINIUM HALIDES AND SODIUM HYDRIDE

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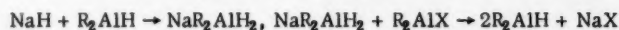
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As we have shown previously, the lower dialkylaluminium halides can readily be obtained by the symmetrization of the available alkylaluminium sesquihalides with sodium halides [1]. The conversion of the dialkylaluminium halides into dialkylaluminium hydrides is of considerable interest since the latter are good reducing agents. Only the conversions of diethylaluminium chloride [2] and diethylaluminium bromide [3] are known. In the present work we have studied the reduction of dimethylaluminium chloride and dimethylaluminium iodide to dimethylaluminium hydride, the reduction of diethylaluminium chloride, bromide, and iodide to diethylaluminium hydride, the reduction of dipropylaluminium chloride and bromide to dipropylaluminium hydride, and the reduction of diisobutylaluminium chloride and bromide to diisobutylaluminium hydride with sodium hydride. The reduction of diethylaluminium chloride with sodium hydride in hexane described by Ziegler et al. [2] takes place slowly and incompletely (it requires repeated treatment with sodium hydride at a temperature of 120-125°). The dialkyl aluminium halides mentioned are rapidly and completely reduced at a temperature of 40-60° to the corresponding dialkylaluminium hydrides using sodium hydride in solution in hydrocarbons, best aromatic hydrocarbons (benzene, toluene), if the reduction is carried out in the presence of a primer of the corresponding dialkylaluminium hydride. A trialkylaluminium may also be used as the primer. The role of the added dialkylaluminium hydride amounts to bringing the sodium hydride into solution in the form of the complex  $\text{NaR}_2\text{AlH}_2$ , which acts as the reducing agent for the dialkylaluminium halide.

Thus, reduction takes place according to the following scheme:



The dialkylaluminium hydride formed also gives a complex with the sodium hydride which reduces a fresh portion of dialkylaluminium halide, and so on. The yield of hydrides amounts to 75-85% of theoretical. The results of the experiments are given in the Table.

$\text{R}_2\text{AlX}$	Yield of corresponding hydrides, %	B.p. of the hydride, °C (p mm Hg)	$\text{R}_2\text{AlX}$	Yield of corresponding hydrides, %	B.p. of the hydride, °C (p mm Hg)
$(\text{CH}_3)_2\text{AlCl}$	84	43 (3)	$(n\text{-C}_8\text{H}_{17})_2\text{AlCl}$	79	94-96 (1)
$(\text{CH}_3)_2\text{AlI}$	72	The same	$(n\text{-C}_8\text{H}_{17})_2\text{AlBr}$	85	—
$(\text{C}_2\text{H}_5)_2\text{AlCl}$	86	65-67 (1)	$(i\text{-C}_4\text{H}_9)_2\text{AlCl}$	70	114 (1)
$(\text{C}_2\text{H}_5)_2\text{AlBr}$	82	—	$(i\text{-C}_4\text{H}_9)_2\text{AlBr}$	80	The same
$(\text{C}_2\text{H}_5)_2\text{AlI}$	87	—			

We also carried out the reduction of ethylaluminium sesquichloride and sesquibromide by sodium hydride in the presence of a primer of diethylaluminium hydride in benzene solution at 50°. The reaction takes place readily and without decomposition of the reaction products; however, an equimolecular mixture of diethylaluminium hydride and ethylaluminium hydride cannot be obtained and generally a mixture containing ~70% of diethylaluminium hydride and 30% of ethylaluminium hydride is formed, obviously through disproportionation of the ethylaluminium hydride.



## EXPERIMENTAL

To a suspension of sodium hydride (3-5% excess) in dry benzene, 1.5-2 g of the appropriate dialkylaluminum hydride or trialkylaluminum was added. After stirring and heating at 70-80° for 15-20 min., the appropriate dialkylaluminum halide was added dropwise to the reaction mixture in such a way that the temperature of the mixture did not exceed 50-60°. After the addition of the halide was completed, the mixture was heated at 50° for 1 hr. The precipitate of sodium halide which separated was filtered off under nitrogen or centrifuged, and washed with a two- or three-fold amount of benzene. The benzene was distilled off in the vacuum of a water jet pump at a bath temperature of 40-50°. The hydride obtained was distilled in vacuum.

Production of a mixture of diethylaluminum hydride and ethylaluminum dihydride from ethylaluminum sesquibromide. To a suspension of 19.1 g of sodium hydride in 300 ml of benzene, 2.3 g of diethylaluminum hydride was added. The mixture was heated at 70-80° for 30 min., after which 102 g of ethylaluminum sesquibromide was added at 50°. Then the mixture was heated for 2 hours at 50-60°. The sodium chloride was separated by centrifuging and washed three times with 100 ml portions of benzene. The benzene was distilled off in the vacuum of a water jet pump. The mixture of hydrides obtained was distilled under a vacuum of 10<sup>-5</sup> mm, and 30 g of a mixture of hydrides was obtained. On decomposition, 0.2880 g of this mixture liberated 250 ml of gas (NTP). Analysis of the mixture of gases showed the presence of 42% of hydrogen, which corresponds approximately to a content of dihydride in the mixture of 30%.

## SUMMARY

Dialkylaluminum halides are readily reduced to dialkylaluminum hydrides by sodium hydride in a hydrocarbon medium in the presence of a primer of the corresponding dialkylaluminum hydride or trialkylaluminum.

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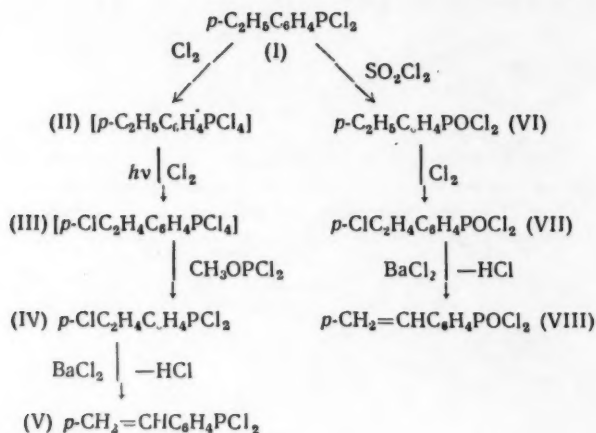
THE DICHLORIDES OF *p*-STYRYLPHOSPHONOUS  
AND *p*-STYRYLPHOSPHONIC ACIDS

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We have recently reported, in association with Chzhan Zhun-yui, the synthesis of the diethyl ester of *p*-styrylphosphonous acid [1] from *p*-styrylmagnesium chloride [2] and diethyl phosphorochloridite. An indication exists [3] that the analogous synthesis of *p*-styryldiphenylphosphine using diphenylchlorophosphine and *p*-styrylmagnesium chloride could not be performed; only a mixture of polymeric products was obtained. *p*-Styryldiphenylphosphine has been synthesized by another route, namely, the dehydration of *p*-( $\alpha$ -hydroxyethyl)-phenyldiphenylphosphine, which was obtained in four stages from *p*-bromoacetophenone. However, Koton, Kiseleva, and Florinskii [4] mention the successful synthesis of *p*-styryldiphenylphosphine from *p*-styrylmagnesium chloride and diphenylchlorophosphine; unfortunately, these authors give no description of the synthesis and the constants of the substance obtained. Recently a paper has been published on the synthesis of *p*-styrylphosphonic acid [5] from  $\beta$ -bromoethylbenzene through a series of stages which include the nitration of this compound, the conversion of the *p*-nitro- $\beta$ -bromoethylbenzene formed into  $\beta$ -chloroethyl-*p*-aminobenzene, diazotization, replacement of the diazo group by a phosphoric residue, and dehydrochlorination of the *p*-( $\beta$ -chloroethyl)-phenylphosphonic acid.

In this paper we shall give an account of the synthesis of the dichlorides of *p*-styrylphosphonous (V) and *p*-styrylphosphonic (VIII) acids, which may be used as convenient starting materials for the production of various phosphorus-containing styrene derivatives.



p-Ethylphenyldichlorophosphine (I) [6], readily obtainable from ethylbenzene and phosphorous trichloride \* is converted by chlorine in chlorobenzene into the corresponding tetrachloride (II) which on further photochemical chlorination, gives p-chloroethylphenylphosphorus tetrachloride (III), apparently as a mixture of the  $\alpha$ - and  $\beta$ -chloro-substituted isomers. We did not isolate this substance in pure form but reduced it directly by the action of methyl phosphorodichloridite [8] to p-chloroethylphenyldichlorophosphine (IV), probably also a mixture of the  $\alpha$ - and  $\beta$ -isomers. Dehydrochlorination of this substance over barium chloride [9] at 450° in vacuum led to the dichloride of p-styrylphosphonous acid (V). The dichloride of p-styrylphosphonic acid (VIII) was synthesized by the following

\*To displace the p-ethylphenyldichlorophosphine from the complex compound with aluminum chloride, pyridine [7] was used, and not phosphoric trichloride [6].

route: *p*-ethylphenyldichlorophosphine (I) was oxidized by the action of sulphuryl chloride [10], with cooling, to the dichloride of *p*-ethylphenylphosphonic acid (VI), which was converted on photochemical chlorination into the dichloride of *p*-chloroethylphenylphosphonic acid (VII), apparently in the form of a mixture of isomers differing in the position of the chlorine atom in the ethyl group. The dichloride (VII) on dehydrochlorination over barium chloride at 450° in vacuum gave the dichloride of *p*-styrylphosphonic acid (VIII), the synthesis of which from ethylbenzene is thus accomplished in four stages.

## EXPERIMENTAL

*p*-Chloroethylphenyldichlorophosphine (IV). A current of dry chlorine was passed over the surface of a stirred solution of 110 g (0.53 mole) of *p*-ethylphenyldichlorophosphine [6] in 150 ml of dry chlorobenzene at a temperature of -5 to 0°. After the separation a pale yellow precipitate and the cessation of the evolution of heat, the temperature of the reaction mixture was raised to 50-60° and chlorine was passed for 15-20 min. while the solution was irradiated with ultraviolet light, the temperature being maintained at 80-90° by means of the heat of the reaction. The chlorination was discontinued after the absorption of 50-60% of the theoretical amount of chlorine necessary to obtain the monochloro derivative. After the completion of the chlorination, the chlorine which had not reacted was removed by passing a current of purified nitrogen through the mixture at 80-90° for 30 min. Then 73 g (0.55 mole) of methyl phosphorodichloridite was added dropwise to the reaction mixture in a current of nitrogen with stirring at 90-100°. The mixture was heated at the same temperature for 30 min., the solvent was removed in vacuum, and the residue was distilled. The yield was 61.5 g (48%, calculated on the initial *p*-ethyldichlorophosphine); it formed a semi-crystalline mass melting completely at 37°; b.p. 105-106° (1 mm);  $n_D^{20}$  1.5985;  $d_4^{20}$  1.3550. Found: C, 40.0, 39.8; H, 3.4, 3.5; P, 12.8, 12.8; Cl, 44.6, 44.2%.  $C_8H_9PCl_3$ . Calculated: C, 39.8; H, 3.3; P, 12.8; Cl, 44.0%.

Dichloride of *p*-styrylphosphonous acid (V). Fourteen grams of *p*-chloroethylphenyldichlorophosphine was passed in 2 hr at 450° in a vacuum of 10-15 mm through a tube filled with granular calcined barium chloride (grain size 2-3 mm); the length of the tube was 70 cm and its diameter 1.6 cm. The drop in pressure between the beginning and end of the tube was 3-4 mm Hg. After four passes through the tube, the reaction mixture was fractionated; the yield of the dichloride of *p*-styrylphosphonous acid was 5.5 g (46%); b.p. 74-75° (1 mm);  $n_D^{20}$  1.6231;  $d_4^{20}$  1.2709. Found: C 46.6, 46.4; H 3.4, 3.5; P 15.0, 15.0; Cl 34.8, 34.2%.  $C_8H_7PCl_2$ . Calculated: C 46.9; H, 3.4; P 15.1; Cl 34.6%.

Dichloride of *p*-ethylphenylphosphonic acid (VI). Two hundred grams (1.48 mole) of sulphuryl chloride was added in drops with vigorous stirring at -10- -20° to 300 g (1.45 moles) of *p*-ethylphenyldichlorophosphine; the thionyl chloride was distilled off, and the residue was distilled in vacuum. The yield of the dichloride of *p*-ethylphenylphosphonic acid was 317 g (98%); b.p. 100-100.5° (1.5 mm);  $n_D^{20}$  1.5521;  $d_4^{20}$  1.2949. Found: C 42.9, 43.0; H 4.1, 4.1; P 13.8; Cl 31.8, 31.5%.  $C_8H_9POCl_2$ . Calculated: C 43.1; H 4.1; P 13.9; Cl 31.8. Literature data [11]: b.p. 294°;  $d_4^{16}$  ~1.29.

Dichloride of *p*-chloroethylphenylphosphonic acid (VII). The chlorination of 346 g of the dichloride of *p*-ethylphenylphosphonic acid was carried out at 80-90° in ultraviolet light until 50-60% of the theoretical amount of chlorine had been absorbed. The reaction mixture was fractionated in vacuum. The yield of the dichloride of *p*-chloroethylphenylphosphonic acid was 180 g (45%); b.p. 123-124° (1 mm);  $n_D^{20}$  1.5663;  $d_4^{20}$  1.4067. Found: C 37.2, 37.5; H 3.2, 3.2; P 12.1, 11.8; Cl 41.8, 42.0%.  $C_8H_8POCl_3$ . Calculated: C 37.3; H 3.0; P 12.0; Cl 41.3%.

Dichloride of *p*-styrylphosphonic acid (VIII). The dehydrochlorination conditions were similar to those described above for *p*-chloroethylphenyldichlorophosphine. After two passes of 12 g of the dichloride of *p*-chloroethylphenylphosphonic acid through the tube, 5.5 g (53%) of the dichloride of *p*-styrylphosphonic acid was obtained; b.p. 102-103° (1.5 mm);  $n_D^{20}$  1.5877;  $d_4^{20}$  1.3412. Found: C 43.3, 43.1; H 3.2, 3.2; P 14.1, 14.2; Cl 31.9, 31.5%.  $C_8H_7POCl_2$ . Calculated: C 43.2; H 3.2; P 14.0; Cl 31.9%.

## SUMMARY

The synthesis of the dichlorides of *p*-styrylphosphonous and *p*-styrylphosphonic acids has been carried out.

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# THE DECOMPOSITION OF PHENYLDIAZONIUM BOROFLUORIDE IN NITROBENZENE IN THE PRESENCE OF ZINC, CADMIUM, AND SILVER POWDERS

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It has been shown earlier [1] that the presence of copper transforms the heterolytic character of the decomposition of aryldiazonium borofluorides into a homolytic one. It was of interest to investigate the action of other metals in this direction also. It has been shown in the present work that the decomposition of phenyldiazonium borofluoride in nitrobenzene in the presence of zinc, cadmium, and silver powders also takes place homolytically, with the formation of products of the interaction of phenyl radicals with the nitrobenzene. The formation in small yield of all three isomeric nitrobiphenyls has been shown in the reaction products, *p*-nitrobiphenyl being isolated in predominating amount. When the decomposition takes place in the presence of zinc and silver, azobenzene is also formed.

In the heterolytic decomposition of aryldiazonium borofluorides in nitrobenzene in the absence of metals [2], the only nitrobiaryl formed is the *m*-nitrobiaryl; again no formation of azo compounds is found. Thus, the presence of zinc, cadmium, or silver, like that of copper, converts the heterolytic mechanism of the decomposition of phenyldiazonium borofluoride into a homolytic one (scheme, see [1]). Consequently, the synthesis of organometallic compounds by the decomposition of aryldiazonium salts in the presence of metals also takes place by a homolytic route. It is interesting to note that the weakly nucleophilic metal silver, being incapable of forming a covalent bond with the cation of an onium halide and causing the subsequent homolytic decomposition of the onium halide [3], is sufficiently nucleophilic to convert the diazonium form of phenyldiazonium borofluoride into the diazo form.

## EXPERIMENTAL

General procedure for the decomposition of phenyldiazonium borofluoride in nitrobenzene in the presence of metals. The phenyldiazonium borofluoride was added in small portions to a suspension of the metal powder in nitrobenzene at room temperature with stirring. Stirring was continued until the test for diazonium ( $\beta$ -naphthol) in the reaction mixture was negative. The lump of resin and the residue of the metal were filtered off and washed with hot benzene. The combined nitrobenzene and benzene filtrates were washed with 10% caustic soda, and water, and water, and were distilled with steam and, finally, with superheated steam. The volatile products from the alkali-washed clump of resin and the metallic residues were also isolated in the same distillation. The steam-distillation



products were fractionated in vacuum and separated by crystallization. The reaction products were identified by determining the melting points of mixtures with known substances.

In the presence of zinc. A mixture of 164 g of phenyldiazonium borofluoride, 415 g of nitrobenzene, and 87 g of zinc powder were mixed as described above. There was no rise in the temperature. The reaction for diazonium was negative after 7 days. The following were isolated: 0.1 g of *o*-nitrobiphenyl, b.p. 95-110° (3 mm), m.p. 36-37° (after sublimation); 0.3 g of *m*-nitrobiphenyl, b.p. 145-150° (3 mm), m.p. 58-59° (after sublimation); 1.04 g of *p*-nitrobiphenyl, b.p. 155-170° (3 mm), m.p. 113-114° (recrystallized from ethyl alcohol and sublimed); and 0.26 g of azobenzene (from methyl alcohol), m.p. 66-68°.

In the presence of cadmium. A mixture of 144 g of phenyldiazonium borofluoride, 360 ml of nitrobenzene, and 56 g of cadmium powder (obtained by precipitation with magnesium turnings from a solution of cadmium chloride, and washed with alcohol and ether) was treated as described above. The initial temperature was 22° and the maximum temperature 36° and afterwards stirring was carried out at room temperature. The reaction was complete after 12 days. The following were isolated: 0.17 g of *o*-nitrobiphenyl, b.p. 110-115° (3 mm); m.p. 35-37° after sublimation; 0.3 g of *m*-nitrobiphenyl, b.p. 145-135° (3 mm), m.p. 57° (recrystallized from methyl alcohol); and 1.03 g of *p*-nitrobiphenyl, b.p. 160-170° (3 mm), m.p. 113-114° after sublimation.

In the presence of silver. A mixture of 164 g of phenyldiazonium borofluoride, 330 ml of nitrobenzene, and 43 g of silver powder (precipitated by zinc dust from a solution of silver nitrate, and washed with alcohol and ether) was treated as described above. No rise in temperature was observed. The reaction for diazonium was negative after 2 months. The following were isolated: (1) 0.05 g of *o*-nitrobiphenyl, b.p. 90-110° (2 mm), uv absorption spectrum (SF-4 spectrophotometer on the Dianov-Klovov system):  $\nu_{\max}$  43,000  $\text{cm}^{-1}$ ,  $\epsilon \cdot 10^{-4}$  1.2; authentic *o*-nitrobiphenyl has  $\nu_{\max}$  43,000  $\text{cm}^{-1}$ ,  $\epsilon \cdot 10^{-4}$  1.6; (2) 0.54 g of *m*-nitrobiphenyl, b.p. 125-150° (2 mm), m.p. 58.5° (recrystallized from heptane); (3) 1.02 g of *p*-nitrobiphenyl, b.p. 160-170° (3 mm); m.p. 112-114° (recrystallized from methyl alcohol); and (4) 0.44 g of azobenzene, m.p. 66° (recrystallized from heptane).

#### SUMMARY

In the presence of powdered zinc, cadmium, or silver, phenyldiazonium borofluoride decomposes homolytically with the formation of all three nitrobiphenyls and, in the case of zinc and silver, with the formation of azobenzene as well.

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# THE OXIDATION OF LOW-MOLECULAR-WEIGHT HYDROXYL COMPOUNDS WITH OXIDES OF NITROGEN

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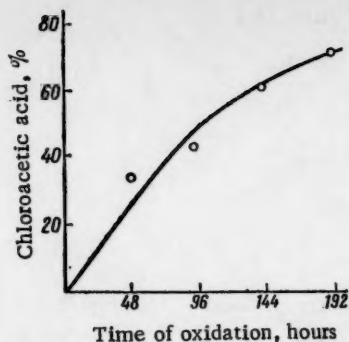
On the basis of experimental data, we earlier concluded that the predominant oxidation with oxides of nitrogen of primary alcohol groups in cyclic carbohydrates and polysaccharides was determined by the I-effect of glucopyranosidic ring [1-4]. Judging from data in the literature, oxidation is not general for primary hydroxyl groups. At room temperature, the lower aliphatic alcohols (methyl, ethyl, etc.) mainly esterify and oxidation is not clearly expressed [5-7]. Investigations carried out in our laboratory [8] showed that the action of oxides of nitrogen in an anhydrous medium led to the formation of only traces of glycolic and oxalic acids from ethylene glycol, while in the presence of water about 1% of oxalic acid was formed. Under these conditions, propane-1,2-diol undergoes practically no oxidation (0.01-0.0025% of hydroxyketone). The results which we obtained and a consideration of the literature data from this point of view [9] permitted us to conclude that the rate of oxidation of primary OH groups is affected by the nature of the substituent (nucleophilic or electrophilic) in the  $\alpha$ -position to the OH group. In oxidation with oxides of nitrogen, a glucopyranosidic ring behaves similarly to an electronegative substituent, i.e., it possesses a definite I-effect and therefore the main direction of the process is the oxidation of the  $\text{CH}_2\text{OH}$  group to a carboxyl group. The absence of clearly expressed electronegative groups in the  $\alpha$ -position to a  $\text{CH}_2\text{OH}$  group ( $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , etc.) leads to the practical disappearance of this reaction. In the present work, we carried out investigations on the oxidation of ethylene chlorohydrin in order to study the influence of the negative effect of the chlorine atom on the velocity of the reaction.

Results of the oxidation of ethylene chlorohydrin with oxides of nitrogen

Concentration of the oxides of nitrogen, M	Time of oxidation, hours	Total yield of chloroacetic acid, % of theoretical	Concentration of the oxides of nitrogen, M	Time of oxidation, hours	Total yield of chloroacetic acid, % of theoretical
0.5	24	5.72	1.0	192	59.80
0.5	48	16.92	1.5	48	34.61
0.5	192	41.15	1.5	92	42.88
1.0	24	18.52	1.5	140	60.00
1.0	48	33.20		192	72.69
1.0	120	52.88	2.0	168	66.34
			2.0	192	74.88

## EXPERIMENTAL

The oxidation of ethylene chlorohydrin with oxides of nitrogen was carried out at room temperature in  $\text{CCl}_4$  solution, the time of oxidation and the concentration of oxides of nitrogen being varied. The ethylene chlorohydrin had b.p. 44-45° (22 mm);  $n_D^{20}$  1.4435. The reaction was carried out in a three-necked flask provided with a reflux condenser, a stirrer, and a dropping funnel. The required amount of oxides of nitrogen in 50 ml of  $\text{CCl}_4$  was added through the dropping funnel to the reaction flask containing a weighed amount of ethylene chlorohydrin (0.25 mole) in 50 ml of  $\text{CCl}_4$ . After 1-2 hours' stirring, the reaction mixture was allowed to stand at room temperature for various times (24-192 hr). An oily layer appeared on the surface of the solution during the oxidation. On completion of the reaction, the excess of the oxides was removed in a vacuum in the cold and the oily layer and an aqueous extract of the carbon tetrachloride layer were investigated for chloroacetic acid by evaporation in vacuum until a precipitate separated. The results of the oxidation are given in the Table.



The chloroacetic acid obtained had b.p.  $104^{\circ}$  (22 mm), which agrees with data in the literature [10]. Found: C 25.52; H 3.26; Cl 37.54%.  $C_2H_3O_2Cl$ . Calculated: C 25.92; H 3.17; Cl 37.56%.

The figures in the Table show that the rate of oxidation of ethylene chlorohydrin increases with an increase in the time of oxidation and the concentration of oxides of nitrogen. A maximum yield of chloroacetic acid of 74.88% was reached at a concentration of oxides of nitrogen of 2 M and a time of oxidation of 192 hr. These experimental results indicate that the presence of a chlorine atom in the  $\alpha$ -position to a  $CH_2OH$  group markedly increases the rate of oxidation of the latter in comparison with that of the lower aliphatic alcohols (methyl and ethyl alcohols, etc.). Thus, after a time of oxidation of 24 hours, ethylene chlorohydrin ( $NO_2 - 1$  M) is 14-18% oxidised, while ethyl alcohol has undergone no oxidation at all [6]. The action of

nitrogen oxides on ethylene chlorohydrin involves the oxidation of the  $CH_2OH$  group with the formation of chloroacetic acid:  $CH_2Cl-CH_2OH \rightarrow CH_2Cl-COOH$ . The oxidation takes place at the same rate as in the case of glucosides and polysaccharides, i.e., the effect of the chlorine atom is similar in this reaction to the effect of a glucopyranosidic ring (Fig. 1).

#### SUMMARY

1. The oxidation of ethylene chlorohydrin by oxides of nitrogen has been studied.
2. The main reaction product is chloroacetic acid, with a maximum yield of 74.88 % of theoretical.
3. The oxidation of the OH group in ethylene chlorohydrin is activated by the negative effect of the chlorine atom to the same degree as the oxidation of glucosides and polysaccharides is activated by the glucopyranosidic ring.

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# 1-CYCLOPROPYL-2- $\alpha$ -FURYL CYCLOPROPANE AND ITS CONVERSIONS

A. P. Meshcheryakov, V. G. Glukhovtsev, and N. N. Le min

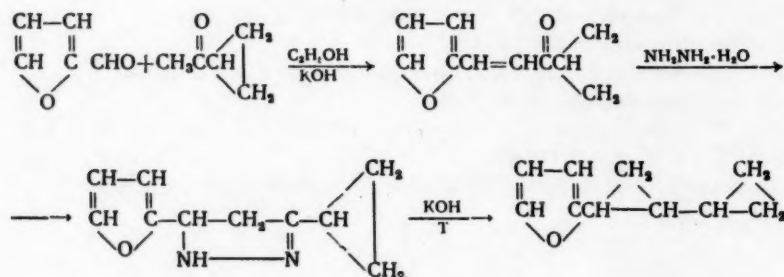
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Original article submitted April 8, 1961

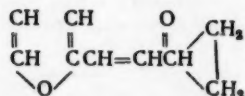
Kizhner was the first to obtain a furane compound containing a cyclopropyl group, namely, 1-methyl-2- $\alpha$ -furylcyclopropane [1]. Later,  $\alpha$ -furylcyclopropane was prepared by a similar route [2]. Several  $\alpha$ -furylmonocyclopropane derivatives have been obtained by the reaction of disodium derivatives of  $\beta$ -ketoesters of the furane series with 1,2-dibromoethane [3]. Furane derivatives with two cyclopropyl groups in the molecule have hitherto been unknown. Methyl cyclopropyl ketone condenses well with benzaldehyde in the presence of alcoholic alkali [4], and somewhat less well with hexahydrobenzaldehyde [5], and it condenses poorly with aldehydes of the aliphatic series possessing a normal structure [5]. Branched-chain aldehydes of the aliphatic series condense with methyl cyclopropyl ketone under the conditions mentioned with low yields [6,7]. In view of this, it was of interest to study the tendency of methyl cyclopropyl ketone to condense with furfural. On hydrogenating  $\alpha$ -furylcyclopropane and 1-methyl-2- $\alpha$ -furylcyclopropane over a palladium catalyst, hydrogenolysis of the cyclopropane ring takes place and the corresponding  $\alpha$ -propyl- and  $\alpha$ -butyltetrahydrofurans are formed [2]. Hydrogenation of the vinyl ethers of methyl and dimethyl cyclopropyl carbinols over Raney nickel takes place without hydrogenolysis of the three-membered ring [3].

In the present work, it was found that hydrogenation of 1-cyclopropyl-2- $\alpha$ -furylcyclopropane over Raney nickel under selected conditions also takes place without hydrogenolysis of the cyclopropyl rings. On oxidizing 1-cyclopropyl-2- $\alpha$ -tetrahydrofurylcyclopropane and 1-cyclopropyl-2- $\alpha$ -furylcyclopropane with  $\text{KMnO}_4$ , 2-cyclopropyl-cyclopropanecarboxylic acid is first produced. We obtained the 1-cyclopropyl-2- $\alpha$ -furylcyclopropane according to the scheme



## EXPERIMENTAL\*

### 1-Cyclopropyl-3- $\alpha$ -furylprop-2-en-1-one

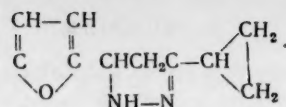


To a mixture of 252.5 g of methyl

cyclopropyl ketone, 10 g of KOH, and 100 ml of  $\text{C}_2\text{H}_5\text{OH}$ , 388.5 g of furfural was added with stirring over 3.5 hours. After 5 hours' stirring, the contents of the flask were poured into 0.5 litre of water and were extracted three times with 150 ml portions of ether. The ether was distilled off and the residue distilled in vacuum. A yield of 462 g (95%) of 1-cyclopropyl-3- $\alpha$ -furylprop-2-en-1-one was obtained with b.p.  $104^\circ$  (2 mm),  $n_D^{20} \sim 1.6075$  (no sharp boundary),  $d_4^{20} 1.1005$ . Found: C 74.00, 74.27; H 6.28, 6.26%.  $\text{C}_{10}\text{H}_{10}\text{O}_2$ . Calculated: C 74.05; H 6.21.

\*The Raman spectra were taken by G. K. Gaivoronskii.

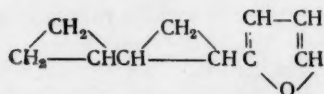
3-Cyclopropyl-5- $\alpha$ -furylpyrazoline.



To 479 g of 1-cyclopropyl-3- $\alpha$ -

furylprop-2-en-1-one in 150 ml of  $C_2H_5OH$ , 147 g of hydrazine hydrate in 75 ml of  $C_2H_5OH$  was added with stirring. After 5 hours' heating at 80-90°, the alcohol was distilled off and the residue was distilled in vacuum. A yield of 492 g (94.5%) of 3-cyclopropyl-5- $\alpha$ -furylpyrazoline was obtained with b.p. 153-154° (14 mm),  $n_D^{20}$  1.5452,  $d_4^{20}$  1.1339. The product was not analysed in view of its instability,

1-Cyclopropyl-2- $\alpha$ -furylcyclopropane

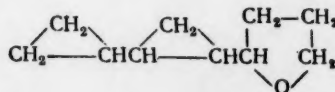


An amount of 490 g of 3-cyclopropyl-

5- $\alpha$ -furylpyrazoline was distilled over 25 g of caustic potash at 191°. After drying with caustic potash and vacuum distillation, 360 g of 1-cyclopropyl-2- $\alpha$ -furylcyclopropane was obtained with b.p. 67° (8 mm),  $n_D^{20}$  1.4972,  $d_4^{20}$  0.9922, yield 87.4%. Found: C 80.29, 80.37; H 7.90, 8.10%; MR 43.91.  $C_{10}H_{12}O$ . Calculated: C 81.03; H 8.15%; MR 44.35.

Raman spectrum ( $\Delta\nu$ ,  $cm^{-1}$ ): 167 (0); 212 (1); 305 (1); 605 (0); 714 (2b); 744 (2b); 815 (3b); 858 (3b); 872 (5b); 917 (3); 942 (2); 973 (1b); 1020 (4b); 1045 (2b); 1076 (4b); 1146 (2b); 1170 (1); 1195 (3); 1208 (1); 1225 (4b); 1239 (1b); 1383 (3); 1407 (1); 1428 (1); 1453 (4); 1506 (10); 1562 (1); 1600 (8); 2875 (1); 2917 (1); 2953 (1); 3010 (10b); 3075 (4).

1-Cyclopropyl-2- $\alpha$ -tetrahydrofurylcyclopropane

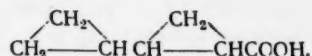


The hydrogenation of

150 g of 1-cyclopropyl-2- $\alpha$ -furylcyclopropane in 150 ml of  $C_2H_5OH$  was carried out in a 1-liter autoclave over 4 g of Raney nickel at 50-65° and a pressure of hydrogen of 100-115 atm. After the absorption of ~40 liter of  $H_2$ , the contents of the autoclave were filtered from the nickel. After the alcohol had been distilled off, the residue was distilled, first in vacuum and then twice in a column. This yielded 60.5 g (39%) of 1-cyclopropyl-2- $\alpha$ -tetrahydrofurylcyclopropane with b.p. 203-203.5 (755 mm),  $n_D^{20}$  1.4700,  $d_4^{20}$  0.9494. Found: C 78.31, 78.51; H 10.57, 10.52%; MR 44.73.  $C_{10}H_{16}O$ . Calculated: C 78.89; H 10.59%; MR 45.31.

Raman spectrum ( $\Delta\nu$ ,  $cm^{-1}$ ): 224 (0); 252 (2); 295 (1); 332 (0); 377 (0); 408 (2 broad); 434 (1); 462 (1); 487 (1); 514 (1); 673 (1); 721 (3); 732 (3); 752 (1); 812 (3 very broad); 874 (3); 923 (5); 954 (0); 995 (1); 1015 (3); 1042 (1); 1132 (2 broad); 1173 (2); 1195 (3); 1230 (10); 1275 (0); 1308 (very broad); 1356 (1 broad); 1390 (1); 1415 (1); 1429 (2); 1447 (1); 1465 (3); 1483 (1); 1510 (1); 1510 (1); 2857 (1); 2873 (5); 2908 (2); 2943 (4); 2971 (4); 3007 (10); 3070 (7).

2-Cyclopropylcyclopropanecarboxylic acid



A 30.5 g batch of 1-cyclopropyl-

2- $\alpha$ -tetrahydrofurylcyclopropane was oxidised with a 1% solution of 126 g of  $KMnO_4$ , which was added in 42 g portions. After conventional working up, 6 g of 2-cyclopropylcyclopropanecarboxylic acid was obtained with b.p. 100° (4 mm);  $n_D^{20}$  1.4730,  $d_4^{20}$  1.0648, yield 25%. Found: C 66.27, 66.19; H 7.96, 8.00%; MR 33.23.  $C_7H_{10}O_2$ . Calculated: C 66.61; H 7.98%; MR 33.19. Acid number found by titration with 0.1 N NaOH: 310; Calculated 326.

Raman spectrum ( $\Delta\nu$ ,  $cm^{-1}$ ): 398 (2b); 447 (1b); 530(1b); 657 (vb); 702 (1); 720 (2); 732 (2); 763 (3); 790 (1); 803 (3); 833 (2); 860 (3); 895 (5 vb); 927 (2b); 951 (1b); 990 (3); 1020 (1); 1049 (2); 1112 (1b); 1127 (1b); 1134 (1b); 1172 (1b); 1192 (5); 1235 (3b); 1295 (vb); 1325 (0); 1368 (1); 1397 (1); 1413 (1); 1428 (2b); 1447 (0); 1460 (2); 1642 (2vb); 2952 (1b); 3013 (10b); 3076 (3).

In the Raman spectrum of cyclopropanecarboxylic acid [9], a frequency of 1645  $cm^{-1}$  indicates the presence of a carbonyl group. In a similar manner, the oxidation of 40 g of 1-cyclopropyl-2- $\alpha$ -furylcyclopropane with 199 g of  $KMnO_4$  yielded 6.5 g of the same acid with a yield of 16%.



## SUMMARY

1. The condensation of methyl cyclopropyl ketone with furfural has yielded 1-cyclopropyl-3- $\alpha$ -furylprop-2-en-1-one, from which 1-cyclopropyl-2- $\alpha$ -furylcyclopropane has been synthesized via 3-cyclopropyl-5- $\alpha$ -furylpyrazoline.
2. 1-Cyclopropyl-2- $\alpha$ -tetrahydrofurylcyclopropane has been obtained by hydrogenation of 1-cyclopropyl-2- $\alpha$ -furylcyclopropane over Raney nickel.
3. Oxidation of 1-cyclopropyl-2- $\alpha$ -furylcyclopropane and 1-cyclopropyl-2- $\alpha$ -tetrahydrofurylcyclopropane has yielded 2-cyclopropylcyclopropanecarboxylic acid.

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## THE MAGNETIC SUSCEPTIBILITY OF DERIVATIVES OF SALICYLALIMINE AND SOME OTHER ORGANIC COMPOUNDS

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In the study of the magnetic susceptibility of complex and internally-complex compounds with complicated organic addends, it is necessary to know the susceptibility of the organic addend. Generally it is calculated by Pascal's method, but it is preferable to have direct experimental data.

We have measured the magnetic susceptibility of a series of organic substances which form complex compounds. The results of these measurements are given in Tables 1 and 2. The figures which we have obtained for the specific and molar susceptibilities of the compounds are given in the third and fourth columns of the Table. The values of the susceptibilities calculated by Pascal's method are given in the fifth column. The sixth column shows for comparison the data in the literature, taken mainly from Tables of constants and numerical data [1].

As can be seen from Tables 1 and 2, the discrepancy between the calculated and experimental values of the magnetic susceptibility is quite considerable. In almost every case, the calculated values are higher than the experimental values in absolute magnitude. Apparently, the additive scheme can be used only with great reservation, since it is impossible for it to reflect all the structural features of compounds having an effect on the magnetic susceptibility. It can be seen that complexity of structure is almost always accompanied by an increase in the difference between the experimental and calculated values of the magnetic susceptibility. As is well known, large deviations from additivity have also been found by other investigators [2,3].



TABLE 1. Magnetic Susceptibility of Derivatives of Salicylalimine

Compound	Formula	Magnetic susceptibility				
		$\chi, g$	$\chi, M$	$\chi_{calc.}$ M	$\chi_{lit.}$ M	$\Delta \chi$
Salicylalimine	$HOC_6H_4 \cdot CH: NH$	0.540	66.1	78.7	69.7	12.6
Salicylalmethylimine	$HO \cdot C_6H_4CHNC_2H_5$	0.560	75.7	90.9	-	15.2
Salicylalethylimine	$HO \cdot C_6H_4CHNC_2H_5$	0.590	88.9	102.3	92.3	13.4
Salicylalbutylimine	$HO \cdot C_6H_4 \cdot CH: NC_4H_9$	0.633	112.2	125.1	-	12.9
Salicylalethylenediimine	$HO \cdot C_6H_4 \cdot CH: N(CH_2)_2NCHC_6H_4OH$	0.577	154.8	176.2	182	21.4
Salicylalhexamethylenediimine	$HO \cdot C_6H_4 \cdot CH: N(CH_2)_6NCHC_6H_4OH$	0.611	198.2	221.8	-	23.6
Salicylalaniline	$HOC_6H_4CHNC_6H_5$	0.605	119.3	129.7	-	10.4
Salicylal-p-nitroaniline	$HOC_6H_4CHNC_6H_4NO_2$	0.527	127.7	147.3	-	19.6
Salicylal-m-nitroaniline	$HOC_6H_4CHNC_6H_4NO_2$	0.526	127.4	147.3	-	19.9
Salicylal-p-toluidine	$HOC_6H_4CHNC_6H_4CH_3$	0.608	128.4	141.9	96.8	13.5
Salicylal-p-anisidine	$HOC_6H_4CHNC_6H_4OCH_3$	0.600	136.4	147.2	122.2	10.8
Salicylal-m-phenylenediimine	$HOC_6H_4CH \cdot NC_6H_4NCHC_6H_4OH$	0.562	177.8	204.4	-	26.6
Salicylal-o-phenylenediimine	$HOC_6H_2CHNC_6H_4NCHC_6H_4OH$	0.566	179.0	204.4	-	25.0

TABLE 2. Magnetic Susceptibilities of Oximes and Some Other Organic Compounds

Compound	Formula	Magnetic susceptibility				
		g	$\chi, M$	$\chi_{calc.}$ M	$\chi_{lit.}$ M	$\Delta \chi$
Dimethylglyoxime	$(CH_3)_2C_2(OH)_2$	0.529	61.4	75.9	63.1	14.5
Salicylaldoxime	$HOC_6H_4CH(OH)$	0.550	75.4	86.0	-	10.6
$\alpha$ -Benzoinoxime	$(C_6H_5)_2C_2(OH)(HOH)$	0.630	137.0	146.4	-	9.4
$\alpha$ -Benzildioxime	$(C_6H_5)_2C_2(OH)_2$	0.560	135.3	153.4	-	18.1
1-2-Cyclohexanedionedioxime	$C_6H_8(OH)_2$	0.554	78.8	93.0	-	14.2
Benzoylacetone	$C_6H_5COCH_2COCH_3$	0.560	90.8	91.4	94.9	0.6
Acetylacetoneimine	$(CH_3)_2CHCl$	0.561	55.6	55.7	-	0.1
$\beta$ -Hydroxynaphthaldehyde	$C_{10}H_6OHCOH$	0.544	93.7	110.7	-	17.0
$\alpha$ -Tribenzoylhydroxylamine	$(C_6H_5CO)_3NO$	0.543	187.4	192.5	-	5.1
$\beta$ -Tribenzoylhydroxylamine	$(C_6H_5CO)_3NO$	0.540	186.4	192.5	-	6.1
Thiophen	$C_4H_4S$	0.684	57.0	57.7	57.5	0.1
Pyrrole	$C_4H_4NH$	0.701	47.0	51.8	47.6	4.8
Aniline	$C_6H_5NH_2$	0.672	62.6	66.0	62.9	3.4
Phenol	$C_6H_5OH$	0.630	59.3	60.3	60.2	1.0
Urea	$CO(NH_2)_2$	0.550	33.4	32.4	33.6	-1.0
Piperidine dithiocarbamate	$C_5H_{10}NCS_2Na$	0.570	104.4	112.2	-	7.8
Diethyl dithiocarbamate	$C_4H_{10}NCS_2Na$	0.610	104.4	104.8	-	0.4

The salicylalimine derivatives, the acetylacetoneimine, the benzoylacetone, and the  $\beta$ -hydroxynaphthaldehyde were given to us by L. A. Kozitsyna and L. L. Polstenko, to whom we express our thanks.

## SUMMARY

1. The magnetic susceptibilities of 30 organic compounds have been measured.
2. The additive scheme for calculation can be used with great reservations. The difference between the experimental and calculated figures generally increase with structural complexity.

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# OXIDATIVE POLYCONDENSATION OF DIACETYLENES

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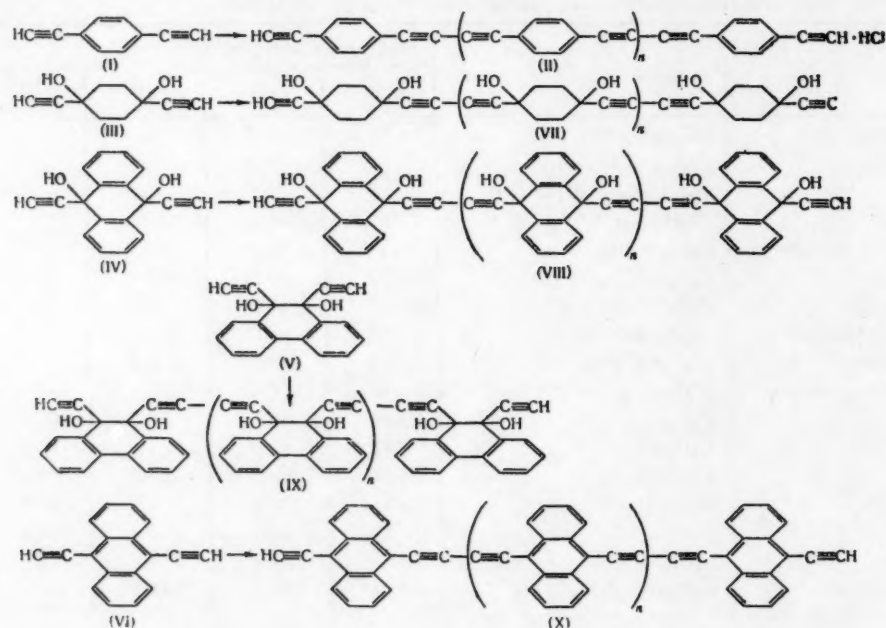
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In one of our papers [1] we have shown, using the example of *p*-diethynylbenzene (I), that the application of oxidative polycondensation to linear diacetylenic compounds may serve as a method for preparing oligomers with conjugated aromatic and acetylenic bonds.\* The poly-*p*-diethynylbenzene (II) synthesized in this way approaches the semiconductors and ferromagnetics in its physical properties [3]. In the present paper the study of this reaction is continued, and by oxidative polycondensation of 1,4-diethynyl-1,4-dihydroanthracene (IV), 9,10-diethynyl-9,10-dihydroxy-9,10-dihydrophenanthrene (V), and 9,10-diethynylantracene (VI) the corresponding polymers were obtained, for which, by analogy with (II), we suggest the structures VII, VIII, IX and X



The initial *p*-diethynylbenzene (I) was obtained by two methods, from the dehydrogenation products of *p*-diethylbenzene [4] and from *p*-diacetylbenzene. The other monomers (III-V) were obtained by the condensation of acetylenes with diketones in liquid ammonia [5]; (VI) was obtained by aromatization of (IV) [6]. Copper (I) chloride was used as catalyst for the polycondensation, and aqueous acetone, aqueous ethanol, and pyridine [2] were used as solvents.

## EXPERIMENTAL

**Bromination of the dehydrogenation products of a mixture of diethylbenzenes.** To 195 g of a mixture of the dehydrogenation products from the diethylbenzenes [4] in 150 ml carbon tetrachloride at  $-12$  to  $-15^{\circ}$  77 ml bromine was added over 4 hr with vigorous stirring. The reaction mixture was stirred for a further 1.5 hr, the precipitated

\*After our report [1] had been published a paper appeared [2] describing an analogous synthesis.

tetrabromides filtered off, washed with 30-40 ml carbon tetrachloride, and recrystallized from chloroform. The yield of tetrabromide depended on the sample of starting material and varied within wide limits from 20 to 50 g; m.p. 156-157°. According to the literature data [7]; m.p. 157°.

Dehydrobromination of p-divinylbenzene tetrabromide was carried out by Deluchat's method [7]. From 22 g of the tetrabromide 4.5 g diethynylbenzene with m.p. 95° was obtained. Literature data: m.p. 95°.

Hydrogenation of p-diacetylbenzene. 45 g p-diacetylbenzene (m.p. 77-79°) in 600 ml ethanol was hydrogenated in the presence of a skeletal nickel catalyst at room temperature and normal pressure. The yield was 86.5% of 1,4-di-(1-hydroxyethyl)benzene (XI), mp. 78.4-80°. Literature data: m.p. 79-81°.

Dehydration of 1,4-di(1-hydroxyethyl)benzene. A solution of 180 g of the diol (XI) in 180 g dioxane was passed during one hour through a catalyst tube containing 50 ml granulated active aluminium oxide. 17.7 g of crude divinylbenzene was obtained and this was used for bromination without further purification.

Bromination of the dehydration product from the diol (XI) was carried out in a similar way to the bromination of the diethylbenzene dehydrogenation products. 35.7 g of the tetrabromide (m.p. 156-157°) was obtained from 15 g crude divinylbenzene.

Oxidative polycondensation of p-diethynylbenzene. To a filtered solution of 3.6 g p-diethynylbenzene (I) in 70 ml dioxane was added a filtered solution of 20 g CuCl, 32 g ammonium chloride and 10 drops of concentrated hydrochloric acid in 100 ml water. Oxygen was passed through the solution and the solution shaken until absorption had ceased completely. The complex was decomposed with water and ether and the oxidation product washed many times with ether. 3.14 g of a reddish orange oligomer (II) was obtained, which did not dissolve in water, alcohol, dioxane, ether, tetrahydrofuran, or other organic solvents. On heating above 120° the oligomer decomposed with the evolution of soot. [3]. Found C 91.54; H 3.81; Cl 4.21% ( $C_{10}H_4$ )<sub>6</sub>H<sub>2</sub>HCl. Calculated: C 91.9; H 3.44; Cl 5.00%. The oligomer did not contain copper.

0.1 g of copper (I) chloride was dissolved in 8 ml dry pyridine and mixed with a solution of 1.3 g p-diethynylbenzene (I) in 8 ml pyridine. The solution was shaken in an oxygen atmosphere at 20° until absorption of the gas had ceased completely. The reaction mass was poured into water, and the separated oligomer washed on the filter with water until Cu<sup>2+</sup> and Cu<sup>+</sup> ions were absent from the wash water. After treatment with hydrochloric acid and water the brilliant yellow oligomer (II) was obtained. It did not contain chlorine or copper. Found: C 93.47; H 3.69%. ( $C_{10}H_4$ )<sub>6</sub>H<sub>2</sub>. Calculated: C 96.5; H 3.54%. ( $C_{10}H_4$ )<sub>6</sub>H<sub>2</sub> · H<sub>2</sub>O. In the working up conditions it is possible that the triple bonds of the oligomer became partially hydrated, and the low analysis for carbon and hydrogen is associated with this.

Oxidative condensation of 1,4-diethynyl-1,4-dihydroxycyclohexane (III). 0.15 copper (I) chloride was dissolved in 10 ml pyridine, and to this solution 1.35 g of glycol (III) in 5 ml of pyridine was added. The mixture was shaken in an oxygen atmosphere until the gas was completely absorbed. Oxidation occurred with the evolution of heat. After working up as described above 1.1 g of a light oligomer (VII) was obtained which was not soluble at room temperature in the normal organic solvents. Found: C 70.75; H 7.00%. Calculated for the monomer: C 73.17; H 7.31%.

Oxidative polycondensation of 9,10-diethynyl-9,10-dihydroxy-9,10-dihydroanthracene (VI). The experiment was carried out in the conditions described above. From 1.6 g of the glycol (IV) was obtained 1.4 g of the polymer (VII) as a dark brown powder which did not contain chlorine but contained traces of copper. Found: C 79.66; H 4.46%. Calculated for the monomer: C 83.05; H 4.69%.

Oxidative polycondensation of 9,10-diethynyl-9,10-dihydroxy-9,10-dihydrophenanthrene (V). The experiment was carried out as described in the previous experiment. The polymer obtained was treated with water and hydrochloric acid to free it from copper and chlorine. From 1.1 g of the glycol (V) was obtained 0.9 g of (IX) as a dark brown powder which did not contain chlorine but contained traces of copper. Found: C 80.54; H 4.16%. Calculated for the monomer: C 83.05; H 4.69%.

Oxidative polycondensation of 9,10-diethynylanthracene. 2.3 g of a black polymer (X), which contained chlorine, was obtained from 2.54 g (VI) after oxidation and the corresponding working up. Found: C 90.96; H 3.83; Cl 1.79%.

## SUMMARY

By oxidative polycondensation of diacetylenic compounds the synthesis of polymers containing diacetylene substituted rings in the molecule was accomplished.

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## SYNTHESIS OF DIQUATERNARY AMMONIUM SALTS OF HEXAMETHYLENEDIAMINE

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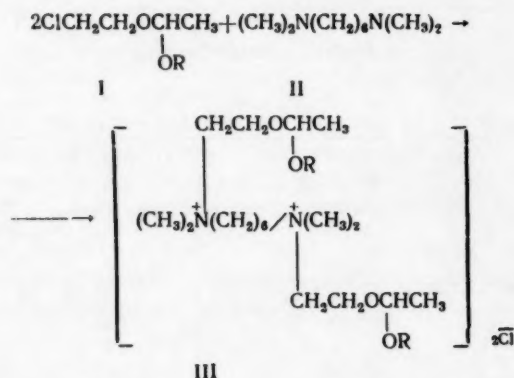
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As is well known quaternary ammonium compounds are used as sensitizers, desensitizers, therapeutic preparations, bacteriocides, disinfectants, conservators, and cation active substances.

In this connection we had the problem of synthesizing the diquaternary ammonium salts (III) which are derivatives of hexamethylene-1,6-bisdimethylamine (II) and the  $\beta$ -chloroethylalkylacetals (I), and the elucidation of the physiological properties of these compounds



where R = C<sub>2</sub>H<sub>5</sub>, n-C<sub>4</sub>H<sub>9</sub>



As we demonstrated previously  $\beta$ -chloroethylalkyl (aryl) acetals (I) are easily symmetrized [1] and hydrolyzed [1], and they exchange the chlorine atom for various alkoxy groups [2] and hydrocarbon radicals [3]. However in the conditions given the reaction proceeds with the formation of the corresponding diquaternary ammonium salts and other modes of reaction are not observed. The diquaternary salts (III) obtained are very hygroscopic solids which dissolve very well in water and alcohol and are not soluble in diethyl ether. The structure of the compounds obtained (III) was demonstrated by their hydrolysis in aqueous solutions at room temperature in the presence of potassium bisulphate without the addition of acid by the method described in [1].

#### EXPERIMENTAL

Diquaternary ammonium salt (III) - derivative of hexamethylene-1,6-bisdimethylamine (II) and ethyl- $\beta$ -chloroethylacetal (I). In a conical flask with a reflux condenser were placed a solution of 7.63 g (0.05 M) ethyl- $\beta$ -chloroethylacetal in absolute ether (1:1) and 4.3 g (0.025 M) hexamethylene-1,6-bisdimethylamine. The mixture was heated on a water bath for an hour. No crystals separated. The reaction mass was sealed in a tube which was heated on a boiling water bath for 20 hr. The product was formed in the ampoule as a glassy mass. It was washed thrice with ether and dried in a vacuum dessicator over sulphuric acid. 2.5 g (21%) of the quaternary salt (III) was obtained.

15.6 g (0.102 M) ethyl- $\beta$ -chloroethylacetal (I) was placed in a conical flask with a reflux condenser and a solution of 8.6 g (0.05 M) hexamethylene-1,6-bisdimethylamine in benzene was added. The reaction mixture was heated on a water bath for 7 hr, when a sticky mass was formed at the bottom of the flask. The reaction mass was cooled, 10 ml of water free ether added, and the mixture stood 12 hr. The ether-benzene solution was removed from the solid crystalline mass which was washed three times with ether and dried in vacuum. The crystalline substance was dissolved in absolute ethanol, precipitated from ethanolic solution with ether and dried in vacuum. The quaternary salt (III) obtained (9.4 g, 39%) was a transparent, very hygroscopic solid mass. Found: Cl 14.85; 14.52; N 6.15%.  $C_{22}H_{50}O_4N_2Cl_2$ . Calculated Cl 14.85; N 5.87%. The salt was 10% hydrolyzed after 1 hr, 39.5% after 17 hr.

Diquaternary ammonium salt (III) ] derivative of hexamethylene-1,6-bisdimethylamine and  $\beta$ -chloroethyl-n-butylacetal. For the reaction a solution of 8.6 g (0.05M) hexamethylene-1,6-bisdimethylamine in benzene (1:1) and 18.2 g (0.101 M) n-butyl- $\beta$ -chloroethylacetal were taken. The mixture was heated on a water bath for 15 hr. A clear sticky mass was formed on the bottom and sides of the flask. After cooling, 10 ml absolute ether were added and the mixture left a day. The ether-benzene solution was separated from the residue; the latter was washed three times with ether and dried in a vacuum dessicator. The quaternary salt (III) obtained (10.68 g, 40.1%) was a slightly yellow solid crystalline mass which was very hygroscopic and dissolved well in alcohol and water. Found: Cl 13.63; 13.18; N 5.69%.  $C_{26}H_{58}O_4N_2Cl_2$ . The salt was 8.75% hydrolysed after 1 hr, 45.5% after 17 hr.

#### SUMMARY

Diquaternary ammonium salts based on hexamethylene-1,6-bisdimethylamine and  $\beta$ -chloroethylalkylacetals have been synthesized.

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# SYNTHESIS OF 1, 10-DECANEDICARBOXYLIC ACID FROM CYCLODODECATRIENE-1,5,9

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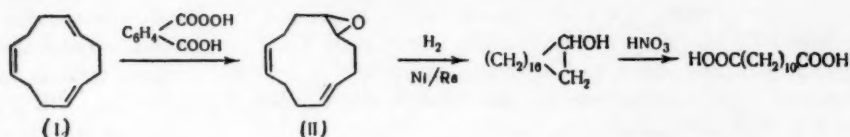
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1,10-Decanedicarboxylic acid is one of the dicarboxylic acids which is difficult to obtain. In this communication we have worked out a simple method (in the preparative sense) for synthesizing this acid from cyclododecatriene-1,5,9 (I), which in turn is easily obtained by the cyclotrimerization of butadiene on a complex organoaluminum catalyst [1]. The synthesis of 1, 10-decanedicarboxylic acid is described by the following scheme



Cis-trans-trans-cyclododecatriene-1,5,9 was easily converted into the monoxide (II) which was hydrogenated over Raney nickel at 140-150° to give cyclododecanol in high yield. The oxidation of cyclododecanol with nitric acid proceeded easily to give 1, 10-decanedicarboxylic acid in 90% yield. The best results were obtained by oxidizing with 60% nitric acid in the presence of ammonium metavanadate.

## EXPERIMENTAL PART

**Preparation of epoxycyclododecadiene-5,9.** An ethereal solution containing 68 g perphthalic acid was added gradually, to a refluxing solution of 100 g cis-trans-trans-cyclododecatriene-1,5,9 in 100 ml ether. After completing the addition the reaction mixture was heated for 4 hr. The ether was evaporated, the residue diluted with 250 ml chloroform, and the phthalic acid filtered off. The chloroform solution was washed with sodium hydroxide solution and water, and dried over potash. On distillation in vacuum 50 g epoxycyclododecadiene was obtained, b.p. 92-93° (1 mm);  $n_D^{20}$  1.5045;  $d_4^{20}$  0.9747 (literature data [2]; 100-101°) plus 3 g diepoxycyclododecane, b.p. 118-120° (1 mm)  $n_D^{20}$  1.5051;  $d_4^{20}$  1.0655. Found: C 74.26; 74.43; H 9.42; 9.39%; MR 54.14.  $C_{12}H_{18}O_2$ . Calculated C 74.23; H 9.28%; MR 54.14.

**Cyclododecanol.** 50 g epoxycyclododecadiene-5,9 dissolved in 100 ml cyclohexane was hydrogenated in the presence of 4.2 g Raney nickel in a liter autoclave at 100 at. and 140-150° for 4 hr. The hot cyclohexane solution was filtered from the catalyst. The cyclohexane was distilled and the solid residue recrystallized from petroleum ether. 45 g Cyclododecanol was obtained, m.p. 79-80°, according to the literature [3]; m.p. 80°.

**1,10-Decanedicarboxylic acid.** 45 ml 60% nitric acid and 0.1 g ammonium metavanadate were heated in a four necked flask fitted with a stirrer, a thermometer and a reflux condenser. The solution was heated to 60° and 10 g cyclododecanol added at such a rate that the temperature of the reaction mixture remained between 60° and 65°. After completion of the addition the mixture was heated for a further 20 min at 60-100°, and was then cooled. The precipitate was filtered off, washed several times with cold water and dried, 10.8 g 1,10-decanedicarboxylic acid, m.p. 125-126° was obtained. According to the literature [4]: m.p. 126.5-127°

## SUMMARY

A simple synthesis of 1,10-decanedicarboxylic acid has been developed, starting from cyclododecatriene-1,5,9.

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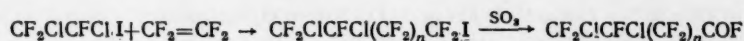
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## FLUORINATED MONOCARBOXYLIC ACIDS

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,  
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Original article submitted April 28, 1961

It has been shown previously [1] that 1,1-dichloro-2-iodotrifluoroethane reacts with oleum to give dichloro-fluoroacetyl fluoride. By extending this reaction to the higher iodo-fluoroalkanes, which are obtained by the telomerization of tetrafluoroethylene with iodo-dichlorotrifluoroethane [3], we have obtained the dichloroperfluoromono-carboxylic acid fluorides



with  $n = 1, 3, 5$ .

As the chain lengthens so the reaction becomes more difficult; thus dichloriodotrifluoroethane reacts with 10% oleum at 100°, 1,2-dichloro-4-iodoperfluorobutane at 150-160°, whereas 1,2-dichloro-6-iodoperfluorohexane and 1,2-dichloro-8-iodoperfluorooctane react only with 45% oleum in an autoclave at 200-250°. The acyl fluorides obtained were converted into anilides and acids.

## EXPERIMENTAL PART

**3,4-Dichloroperfluorobutyryl fluoride.** Into a two-necked flask, fitted with a stirrer and a reflux condenser connected with a descending condenser, were placed 57 g (0.15 M) 1,2-dichloro-4-iodoperfluorobutane and 150 ml 10% oleum (s.g. 1.86). The mixture was stirred and heated on an oil bath at 150-160° for 1 hr. 33.6 g of liquid were collected in the trap. On redistilling this liquid 25 g of dichloroperfluorobutyric acid was obtained, 67.7% yield; b.p. 73-74°. Found: C 19.28; F 44.97%.  $\text{C}_4\text{F}_6\text{Cl}_2\text{O}$ . Calculated: C 19.28; F 45.78%.

The first fraction (3.9 g, b.p. 40.73°) consisted of a mixture of 1,2-dichloro-4-iodoperfluorobutane and 3,4-dichloroperfluorobutyryl fluoride. Unreacted dichloriodoperfluorobutane remained in the residue. The anilide of 3,4-dichloroperfluorobutyric acid has m.p. 64-65° (from pentane). Found: C 37.23; H 1.94; F 28.69; N 4.63%.  $\text{C}_{10}\text{H}_6\text{F}_5\text{Cl}_2\text{NO}$ . Calculated: C 37.27; H 1.86; F 29.50; N 4.35%.

**3,4-Dichloroperfluorobutyric acid.** 7.5 g (0.03 M) 3,4-dichloroperfluorobutyryl fluoride was added gradually with stirring to 20 ml 20% potassium hydroxide. The solution was acidified with 50% sulfuric acid, the layers separated and dried over magnesium sulfate. The aqueous acidic solution was extracted with ether. On distillation 6.1 g 3,4-dichloroperfluorobutyric acid was obtained: yield 83.4%; b.p. 178-179°;  $n_D^{20}$  1.3470;  $d_4^{20}$  1.710; found MR 32.98; calculated for  $\text{C}_4\text{HF}_5\text{Cl}_2\text{O}_2$ , MR 32.65; neutralization equivalent found 246.3, calculated 247.0. Found: C 19.14; 19.19; H 0.33; 0.32%.  $\text{C}_4\text{HF}_5\text{Cl}_2\text{O}_2$ . Calculated: C 19.43; H 0.40%. The anilinium salt has m.p. 108-109° (from dichloroethane). Found: C 35.43; H 2.33; F 28.38; N 4.20%.  $\text{C}_{10}\text{H}_8\text{F}_5\text{Cl}_2\text{NO}_2$ . Calculated: C 35.29; H 2.35; F 27.94; N 4.12%.

**Methyl 3,4-dichloroperfluorobutyrate** 3.7 g (0.015 M) 3,4-dichloroperfluorobutyryl fluoride was added to 10 ml absolute methanol. The reaction mixture was heated for 2 hr on a water bath and then diluted with water. The lower

layer was separated, washed with water, sodium bicarbonate solution, and again with water, dried over calcium chloride, and distilled. 3.1 g Methyl 3,4-dichloroperfluorobutyrate was obtained; yield 80%, b.p. 143°;  $n_D^{20}$  1.3692;  $d_4^{20}$  1.585. Found: C 23.50; 23.36; H 1.22; 1.16%; MR 37.07.  $C_5H_3F_5Cl_2O_2$ . Calculated: C 23.00; H 1.15%; MR 37.37.

**5,6-Dichloroperfluorocaproic acid.** 16 g 5,6-dichloro-1-iodoperfluorohexane and 10 ml 45% oleum (s.g. 1.98) were placed in a 50 ml steel ampoule. The ampoule was sealed and heated at 100° for 7 hr. The contents of the ampoule were emptied into a separating funnel, the upper light layer separated, and distilled. A fraction was separated with b.p. 115-130°. A second distillation gave 5,6-dichloroperfluorocaproyl chloride, b.p. 117-118°. Neutralization equivalent; found 181; calculated for  $C_6F_{10}Cl_2O$  174.5. Ionic fluorine; 4.47%. The anilide has m.p. 84° (from heptane). Found: C 34.19; 33.91; H 1.90; 1.96; F 40.11; 40.36%.  $C_{12}H_6F_9Cl_2NO$ . Calculated: C 34.12; H 1.42; F 40.52%.

In another similar experiment the product was separated, washed with water, and treated with sodium bicarbonate solution. The unreacted dichloriodoperfluorohexane (2 g), which did not dissolve in the sodium bicarbonate, was separated. The bicarbonate solution was acidified with 50% sulfuric acid and extracted with ether. The ether extract was dried with magnesium sulfate, the ether evaporated, and the residue distilled in vacuum. 6.6 g 5,6-dichloroperfluorocaproic acid was obtained; yield 65%, based on dichloriodoperfluorohexane consumed; b.p. 138° (63 mm); m.p. ~10°;  $n_D^{20}$  1.3612;  $d_4^{20}$  1.814; found MR 42.34; calculated for  $C_6HF_9Cl_2O_2$  MR 42.43; neutralization equivalent found 343.4; calculated 347.0. Found: C 20.80; 21.27; H 0.70; 0.44; F 50.69; 50.30%  $C_6HF_9Cl_2O_2$ . Calculated C 20.75; H 0.29; F 49.28%. The anilinium salt has m.p. 84° (from dichloroethane). Found: C 32.91; 32.88; H 1.76; 1.96; F 37.88; 37.95%.  $C_{12}H_6F_9Cl_2NO_2$ . Calculated C 32.73; H 1.82; F 38.86%.

**7,8-Dichloroperfluorocaprylic acid.** In a similar way 7,8-dichloroperfluorocapryloyl fluoride, b.p. 160-161°, was obtained by heating 22 g (0.037 M) 7,8-dichloro-1-iodoperfluorooctane with 15 ml 45% oleum at 250° for 16 hr. Found: C 20.99; 21.00; F 58.37; 57.07%.  $C_8F_{14}Cl_2O$ . Calculated: C 21.38; F 59.24%.

The acyl fluoride was hydrolyzed and the ionic fluoride determined thiorimetrically; found 3.45%; calculated for  $CF_2ClCFCl(CF_2)_6COF$  4.23%. The anilide has m.p. 114° (from dichloroethane). Found: C 33.01; 32.85; H 1.12; 1.13; F 46.19; 45.65%.  $C_{14}H_6F_{13}Cl_2NO$ . Calculated: C 32.19; H 1.15; F 47.32%.

7,8-Dichloroperfluorocaprylic acid was obtained in 65.5% yield, calculated on 7,8-dichloro-1-iodoperfluorooctane consumed; b.p. 155° (58 mm); m.p. 51°. Neutralization equivalent found 449.9, 451.2; calculated 447. Found: C 21.09; 21.19; H 0.36; 0.34; F 53.12; 53.96%.  $C_8HF_{13}Cl_2O_2$ . Calculated: C 21.47; H 0.23; F 55.26%. The anilinium salt has m.p. 109° (from benzene). Found C 31.77; 31.93; H 1.17; 1.32; F 44.88; 45.36; N 2.56; 2.57%.  $C_{14}H_6F_{13}Cl_2NO_2$ . Calculated: C 31.11; H 1.48; F 45.74; N 2.59%.

#### SUMMARY

1. Fluorinated aliphatic acid fluorides have been formed by the action of oleum on iodofluoroalkanes having a  $CF_2I$  end group.

2. Dichloroperfluoro-butiric, -caproic, and -caprylic acids have been prepared.

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USE OF THE REACTION BETWEEN DILITHIOORGANIC COMPOUNDS  
AND METAL HALIDES TO SYNTHESIZE POLYMERS WITH A CON-  
JUGATED SYSTEM OF DOUBLE BONDS

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

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It is known that diphenyl is formed in almost quantitative yield by the reaction of phenyl-magnesium halides with salts of metals with variable valency



It has been shown that reactions of this type do not go through a radical stage [2]. In this connection it appeared possible to use this reaction for the preparation of polymers from the corresponding difunctional organometallic compounds.

In the literature there are data on the possibility of synthesizing oligophenylenes by the reaction of O-dilithio-benzene with heavy metals halides [3]. We have obtained polymers with a conjugated bond system by the reaction of p-dilithiobenzene, p,p'-dilithiobiphenyl, and dilithiotetraphenylbutadiene-1,3 with titanium, vanadium, and cobalt halides. The polymers formed in this way are powdery products with a color from dark yellow to brown and which are partially soluble in chloroform and benzene; yield 60-70%. The polyphenylenes obtained did not melt up to 450° and contained a crystalline fraction, according to X-ray analysis.

The reaction of dilithiotetraphenylbutadiene-1,3 with arsenic, antimony, and tin halides led to the corresponding heteroderivatives of tetraphenylcyclopentadiene [4]. As we have shown, the use of such halides as titanium tetrachloride, vanadium tetrachloride, vanadium oxychloride and cobalt (II) chloride led to the formation of polydiphenylacetylenes, with a limited solubility in chloroform, in yields of up to 70%. The soluble fraction (vanadium oxychloride reaction) had an orange color, was crystalline, and melted at 220-240°; the number average molecular weight, which was determined with the help of thermistors, was  $1560 \pm 40$ . The insoluble fraction of polydiphenylacetylene was highly crystalline and melted at 390-400°. All the above mentioned polymers gave sharp EPR signals corresponding to  $10^{17}$ - $10^{19}$  paramagnetic particles/g. This agrees with the literature data on polyphenylenes and polydiphenylacetylenes prepared by other methods [5].

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# STRUCTURE OF THE COMPLEX COMPOUNDS OF DIPHENYL-BORON CHLORIDE WITH PRIMARY AMINES

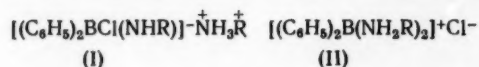
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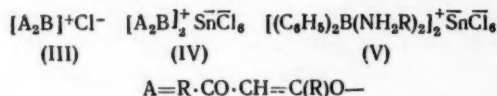
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 10, p. 1913, October 1961

Original article submitted July 26, 1961

We have previously [1] obtained complexes of diphenylboron chloride with two molecules of primary aliphatic amines,  $(C_6H_5)_2BCl \cdot 2NH_2R$ , to which one may ascribe the structure of a borinic (I) or a boronic salt (II)



The only cationic complexes of boron known at present are (III) which Dilthey [2] obtained by the reaction between 1,3-diketones and  $BCl_3$ , and the "diammoniate of diborane" [3]. A characteristic property of (III) is its ability to add metal halides, for example stannic chloride, to form the salt (IV). We found that the complexes of diphenylboron chloride with primary amines behaved towards  $SnCl_4$  in the same way as the complex (III), and on this basis one must describe them as compounds of the boronic type (II).



From the complex of diphenylboron chloride with methylamine (II) ( $R = CH_3$ ) and  $SnCl_4$  in chloroform the complex (V) ( $R = CH_3$ ) was obtained. This complex crystallized from chloroform-pentane as colorless plates. It began to decompose at  $200^\circ$ . Found: C 41.83; H 5.45; N 7.22; Cl 26.90; B 2.88; Sn 14.73%.  $C_{28}H_{40}N_4Cl_6B_2Sn$ . Calculated: C 42.78; H 5.13; N 7.12; Cl 27.10; B 2.75; Sn 15.12%.

The complex (V) ( $R = C_2H_5$ ) was obtained from the ethylamine complex of diphenylboron chloride and  $SnCl_4$ . It crystallized from chloroform-pentane as flat needles which coalesced at  $135^\circ$ . Found: C 44.91; H 5.63; N 6.54; Cl 24.64; B 2.49; Sn 14.34%;  $C_{32}H_{48}N_4Cl_6B_2Sn$ . Calculated: C 45.64; H 5.74; N 6.66; Cl 25.29; B 2.56; Sn 14.10%.

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# SYNTHESIS OF DL-19-NOR-D-HOMOTESTOSTERONE AND ITS 17a-ALKYLHOMOLOGS

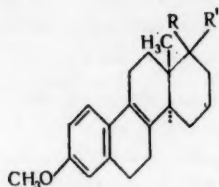
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,  
No. 10, pp. 1913-1914, October 1961  
Original article submitted August 1, 1961

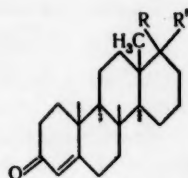
By the reduction of 3-methoxy- $\Delta^{1,3,5,8}$ -D-homoestratetraenone-17a (I) (described by us earlier [1]) with  $\text{LiAlH}_4$  the corresponding carbinol (II) was obtained; yield 88%; m.p. 116-117°;  $\lambda_{\text{max}}$  (in ethanol) 274 m $\mu$  ( $\lg \epsilon$  4.21); acetate-m.p. 154-155°. Reduction of the carbinol (II) by Burch's method followed by acid hydrolysis led to DL-19-nor-D-homotestosterone (III); yield 50%; m.p. 140-141°  $\lambda_{\text{max}}$  241 m $\mu$  ( $\lg \epsilon$  4.21); IR-spectrum 1662, 1669  $\text{cm}^{-1}$ ; propionate (IIIa) m.p. 111-112°;  $\beta$ -phenylpropionate (IIIb) m.p. 141-143°.

By the reaction of the ketone (I) with  $\text{CH}_3\text{MgI}$  a mixture of carbinols was obtained, from which were separated 39% 17a  $\beta$ -carbinol (IV) with m.p. 114-115° and 44% 17a  $\alpha$ -carbinol (V) with m.p. 126-127°. Birch reduction of the carbinol (IV) followed by hydrolysis gave DL-17a-methyl-19-nor-D-homotestosterone (VI); yield 39%; m.p. 171-3°; IR-spectrum 1670  $\text{cm}^{-1}$ .

Ethynylation of the ketone (I) led to the ethynylcarbinol (VII) (yield 72%, m.p. 154-156°) which on hydrogenation gave the ethylcarbinol (VIII); yield 75%, m.p. 181-2°.



- (I)  $R + R' = O$   
(II)  $R = H; R' = \beta\text{-OH}$   
(IV)  $R = \alpha\text{-CH}_3; R' = \beta\text{-OH}$   
(V)  $R = \beta\text{-CH}_3; R' = \alpha\text{-OH}$   
(VII)  $R = C \equiv CH; R' = OH$   
(VIII)  $R = C_2H_5; R' = OH$



- (III)  $R = H; R' = \beta\text{-OH}$   
(IIIa)  $R = H; R' = \beta\text{-OCOC}_2\text{H}_5$   
(IIIb)  $R = H; R' = \beta\text{-OCOCH}_2\text{CH}_2\text{Ph}$   
(VI)  $R = \alpha\text{-CH}_3; R' = \beta\text{-OH}$   
(IX)  $R = C_2H_5; R' = OH$

Birch reduction of the latter, followed by hydrolysis, led to DL-17a-ethyl-19-nor-D-homotestosterone (IX) (configuration at  $C_{17a}$  not established); yield 52%; m.p. 152-154°  $\lambda_{\text{max}}$  241 m $\mu$  ( $\lg \epsilon$  4.23); IR spectrum 1667  $\text{cm}^{-1}$ . The compounds (III), (IIIa), (IIIb), (VI) and (IX) have anabolic effects at low androgenic activity; the ketol (VI) has the best index.

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## CURRENT EVENTS

### GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCE OF THE ACADEMY OF SCIENCES, USSR, April 28, 1961

Translated from the Bulletin of the Academy of Sciences  
USSR, Division of Chemical Sciences,  
No. 10, pp. 1915-1919, October 1961

The 28th of April, 1961, witnessed the general meeting of the Division of Chemical Science of the Academy of Sciences, USSR, at which was heard a report of Academic Secretary of the Division of Chemical Science Academician N. N. Semenov "Measures for Executing the Resolution of the Central Committee of the Communist Party of the Soviet Union and the Council of Ministers, USSR, of April 3, 1961, and titled 'Measures for Improving Coordination of Scientific Research Work in the Country With the Activity of the Academy of Sciences, USSR' ", as well as a discussion of the responsibilities of the institutes of the division to the XXII meeting of the Communist Party of the Soviet Union.

In his report, N. N. Semenov pointed out, that the socialist social structure opens completely unseen possibilities for the development of science and technology, and for the elevation on this basis of the well-being of society. However, we are still not completely using all the advantages provided by the socialist system, we do not always work with sufficient sense of purpose and single mindedness on the solution of the more important problems of science, we are only slowly impressing the achievements of science on the People's Economy. There are deficiencies in the preparation and use of the scientific workers of the institutes of the Academy of Science, the branch institutes, and the institutions of higher learning. Now that the importance of science has grown immeasurable, now that science has become one of the principal factors of social progress, it is impossible to tolerate the existing deficiencies. The resolution of the central committee of the Communist Party of the Soviet Union and the Council of Ministers, USSR, of April 3 of this year will make it possible for us to rise to a new level of organization of science, it increases the responsibility of the Academy of Sciences, USSR, for the development of social and natural sciences in our country, it obliges us to remove all the existing deficiencies in the organization of science.

N. N. Semenov reported on the problems and structure of the newly organized committee on coordination of scientific research, and called on the scientists of the division to give active aid to the organization and day-by-day activity of the committee and its sections. In this connection the speaker pointed out a number of concrete deficiencies of organization in the coordination and planning of research in the institutes of the Academy of Sciences, USSR, and showed the way to remove them. In particular, he pointed out the slowness of development of the work on inorganic polymers, on biologically active materials for agriculture, on problems of separation and purification of monomers, on the chemistry of cellulose, on problems of polymer working etc.

The speaker devoted particular attention to the problems of preparing staffs, and in particular, to the problem of organizing a system of scientific training periods. In conclusion, N. N. Semenov called on the scientists of the institutes of the division to consider, in professional councils among wide groups of workers, with the participation of young scientific co-workers, questions regarding the selection of the principal directions of work, improvement of the coordination of research, and removing the existing deficiencies. The debates after the report of the academic secretary of the division were participated in by academicians: A. E. Arbuzov, A. P. Vinogradov, A. A. Balandin, B. A. Kazanskii, V. I. Spitsyn, and corresponding members of the Academy of Sciences; B. V. Deryagin, N. K. Kochetkov, V. V. Korshak, M. M. Koton, A. A. Korotkov, N. A. Toropov, B. G. Levich, Doctors of Science: F. F. Vol'kenshtein, N. D. Tomashov, M. F. Shostakovskii et al. With striking unanimity they welcomed the measures taken by the Party and the government, directed toward improving the activities of the Academy of Sciences, and reported on the concrete measures which are being taken in the institutes in connection with the resolution. In a number of instances questions were discussed dealing with accelerating the application of results of research, with improving the coordination of scientific research and various concrete problems giving examples of good and bad work by scientific councils. The most important scientific problems were named, in which it is a first order of importance to establish active cooperation. The directors of the institutes in their presentations spoke at one and the same time of the important

obligations which had been assumed by the scientific co-workers of the institute to the XXII meeting of the Communist Party of the Soviet Union, and the measures which were being taken in the institutes to insure meeting the obligations assumed.

After discussion the following resolution was adopted by the general meeting of the Division of Chemical Science of the Academy of Sciences, USSR:

1. To recommend that the Directors of the institutes continue the work begun in reviewing the lines of work and structure of the institutes, curb low priority work so that scientific man-power can be applied to the solution of problems which have large scientific importance in the national economy. To consider the expediency of calling more widely upon the community of the institute for solving this problem.

2. To recommend to the Bureau of the Division periodic discussions in extended sessions of the Bureau on the reports of the Directors of the institutes concerning the results achieved by the institutes in the activity in question.

3. To consider the expediency of again making an official request to the directive organizations regarding the introduction of a system of training periods in the Academy of Sciences, USSR, for the purpose of making the maximum use of the scientists of the academy in the training of high quality research staffs, as well as providing a better selection of scientific workers for the institutes of the Academy of Sciences, USSR.

4. To recognize the obligations of the scientific workers of the institutes to the XXII meeting of the Communist Party of the Soviet Union. To commission the Directors of the Institutes and the Bureau of the Division to take under special observation the fulfillment of these obligations.

GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCE  
OF THE ACADEMY OF SCIENCES, USSR, JUNE 22, 1961

The Scientific session of the general meeting of the Division of Chemical Science of the Academy of Sciences, USSR, on June 22, 1961, was devoted to questions in the chemistry of polymers.

The first paper on the subject: "Polymerization in the Ordered State" was given by Academician V. A. Kargin. He noted that in recent years, work in the field of polymerization has more and more often been pursuing two goals: preparation of polymers with a regular structure of the chain molecules, and successful polymerization of new substances containing multiple bonds which do not polymerize under ordinary conditions. The solution of both these problems is facilitated by preliminary ordering of the molecules of the substances to be polymerized by converting them into the solid state by condensation on the surface of solid bodies, or by using liquid media having very well-marked close order. It is particularly important to reduce the entropy of the monomeric substance when it is being ordered, for this makes it possible to polymerize a number of substances, the polymerization of which in the liquid state is thermodynamically impossible.

Polymerization in the solid state was accomplished by adding initiating substances to the solid monomer by combined condensation of the vapors of the monomer and the initiating substances on a surface, cooled by liquid nitrogen. From the use of a wide range of initiating substances and monomers it was observed that polymerization in the solid state can occur at explosive rates at very low temperatures. In these cases the polymerization occurs during phase transformations in the solid monomer which provide a sufficient amount of molecular mobility. In particular, it was possible under these conditions to achieve the polymerization of acetone. It was found that polymerization in the solid state can occur at high rates even without phase transformations in the mass of the polymer. As examples of reactions of this sort, the speaker cited the polymerization of solid salts of acrylic acid, initiated by chemical exchange reactions in contact with other solid salts, and by mechanical dispersion, as well as polymerization of metacrylamide by crushing the solid monomer in the presence of salts. In these systems the molecular mobility of the monomer is caused by the formation of defects in the solid body, which multiply as the polymerization develops. The speaker and his coworkers observed that an increase in polymerization rate is noted even in sorption layers. However, judging from the example of the polymerization of acrylic acid, sorbed on a number of insoluble salts and silical gel, one could conclude that heterogeneous catalysis of this sort occurs only when the sorbing surface itself is a polymerization initiator. Very active ordering agents are to be found among many inorganic salts, which form complexes with the monomers both in the solid state, and in saturated solutions. In salt media of this sort such as zinc, beryllium, aluminum chloride, etc., it was found possible to polymerize nitriles, as a result of the multiple bond between carbon and nitrogen, and the formation of polymers with alternating atoms of nitrogen and carbon in the main valence chains. The polymers prepared are typical polymers, containing conjugated double bonds. They are semiconductors, and decompose only at a very high temperature. The polymerization reaction occurs as a step process, caused by small quantities of protonic acids. In salt media of this sort it was possible to effect polycondensation of acetone likewise with the formation of a polymer having conjugated double bonds. Under similar conditions complex-forming additives produce stereo-regularity in the polymerization process, which has been shown in the case of methyl methacrylate.

Academician S. S. Medvedev in his paper on the subject: "Some Problems of Carbanion and Catalytic Polymerization" reported, that one of the most interesting problems in the field of ionic and catalytic polymerization is the method of regulating the development (growth) reactions of the polymerized chains, which is what, for a given set of monomers, determines the structure of the chains and the properties of the polymers being formed. A fundamental characteristic of the development of ionic polymerization is the presence on the end of the growing polymer chain of an ionic pair, consisting of an anion or cation located in a field of ions opposite to it. Therefore, it seemed that in the case of ionic polymerization regulation may be effected by changing the nature and structure of the opposite ions, which, in the majority of cases, are parts of the original initiators. However, the data existing in this field indicate that this possibility is very limited. Thus, it follows from the results obtained from the study of cation polymerization, that the effect of the counter ion on the direction of the chain growth reactions is very small, although rupture reactions and degeneration of chain transmission depend on the nature of the counter ion. More definite results were obtained from the study of anion polymerization. The most interesting and fundamental



results were obtained from the study of polymerization in the presence of alkali and metals in their organic compounds. In particular, it was shown that the composition of co-polymers and the structure of diene polymers depends on the nature of the alkali metals and varies in a regular way depending on the nature of the solvents. Two important facts are derived from a consideration of the experimental material obtained: 1) lithium and its organic compounds behave very differently from the other alkali metals and their compounds and 2) in passing from hydrocarbon media to electron donor solutions, the difference in behaviour of these metals is considerably ironed out.

This indicates that two different mechanisms exist, which are especially pronounced in non-polar hydrocarbon media. The first mechanism is anionic, characterized by separation of charges in the active group, and predominates in reactions initiated by potassium or sodium and their organic compounds. This is a mechanism followed by reactions under the influence of lithium and its organic compounds in strongly electron donor media. The second mechanism, which occurs in polymerization by lithium and its compounds, has to do with the properties of lithium (the weak polarity of the Li-C bond, and its ability to form side chain bonds with electron donor molecules). In this case the chain growth reaction occurs by interaction of the monomer, both with the carbanion and with the lithium component of the active group of the growing chain. This causes increased selectivity in regard to the union of the monomer molecules with the growing polymer chain.

One of the interesting peculiarities of lithium polymerization is the formation of mutually associated "living" polymers. The degree of association is reduced as the concentration of active centers is reduced, and depends on the nature of the monomers and the electron donor properties of the medium. The associative phenomena have a considerable effect on the reaction kinetics. Deviations are observed from the proportional relation between the polymerization rate and the catalyst concentration, along with an increase in the values of the polymerization activation energy, etc. From the point of view of working out methods for directing the combination of the monomer molecules with the growing polymer chain, considerable interest is presented by the use of Zigler-Natt type catalyst. The advantage of these systems consists in the fact, that there is a ready-made bridging complex in them, which regulates the acts in the development of the polymer chains. In order to explain some of the questions in this field the speaker had carried out some studies on the heterogeneous catalytic polymerization of ethylene in the presence of various monomeric additives, which do not polymerize under the conditions of the experiment, as well as on homo- and co-polymerization of styrol and isoprene in the presence of the catalyst  $\alpha = \text{TiCl}_3\text{-AlR}_3$ .

Consideration of the results obtained on the basis of the model first proposed by Patat, which at the present time forms the basis of a large part of the investigations in this field, enables the speaker to draw a number of conclusions: Polymerization of this type does not show the properties which are characteristic of anionic polymerization. The aluminum component of the catalyst cannot be regarded as an electron acceptor center, since the lowest governing complex formation of monomers with the catalyst are found to be at variance with the sequence observed in the complex formation of these monomers in the presence of Lewis-type acids. The polymerization occurs on the catalyst surface passing through a stage of complex formation between the monomers and the titanium component of the catalyst, with subsequent penetration of the polarized molecule at the Al-C bond. A consideration of the relationships obtained from the study of separate and combined polymerization, along with the adsorptive phenomena, made it possible to find an expression for the combined polymerization of the monomers investigated, analogous to the well-known differential composition equation for radical polymerization, with a slightly changed meaning of the co-polymerization constants, and to evaluate the relative reactivity of the monomers investigated in these reactions.

Prof. M. B. Neiman and A. L. Buchachenko gave a paper on the subject: "Stable Antioxidant Radicals and Their Reactions". The speakers recalled that in 1900 Gomberg discovered the existence of free thermodynamically stable radicals, which occur in equilibrium with their own dimers. Later, three kinetically stable radicals were discovered, which are not in equilibrium with their own dimers. The kinetically stable free radicals are formed in different chemical reactions, for example by taking hydrogen from molecules. By removing hydrogen from the hydroxyl of phenol antioxidants a number of free phenoxy radicals may be prepared. A number of these radicals were prepared by Ley in Zigler's and Bikensol's laboratory in Manchester by oxidizing phenol antioxidants with lead peroxide. The speakers had prepared about 20 phenoxy radicals by oxidizing phenols with organic peroxides and percarbonates in hydrocarbon solutions. These radicals may be observed by means of electron paramagnetic resonance spectra (EPR). The hyper-fine structure of the EPR spectra makes it possible to find the distribution of spin density in the radical. Oxidizing aramines gave more than 20 stable radicals with characteristic EPR spectra. The phenoxy radicals are able to remove hydrogen from the solvent. The rates and activation energies of a number of these reactions were measured experimentally. It was shown that the anti-oxidants not only break the chains, but can also initiate oxidation. Since the lifetime of the free radicals is considerably larger than the time required to carry out physical and



chemical operations, physical and chemical experiments may be made with stable radicals just as with ordinary molecules. For example, the stable anti-oxidant radicals can easily be distilled over, and are reduced on a mercury drop cathode. The absorption spectra of the radicals lie in the visible region. The speakers pointed out that the radicals may be separated from one another and from molecules by chromatographic methods. Several radicals had been separated from mixtures in this way and their structure determined. The EPR method was successful in showing that in the oxidation of polypropylene, stabilized with a phenol anti-oxidant, at the very beginning of the process the anti-oxidant is oxidized to form a phenoxy radical which enters into a number of subsequent reactions. The EPR method was also used to study a number of reactions of anti-oxidant radicals with various molecules. In particular, it was shown that diphenyl nitrogen unites with the molecule of tetramethylthiuramdisulfide with formation of a bond between nitrogen and sulphur.

It was also shown that some cases of mutual strengthening of anti-oxidants may be explained by the fact that the radicals formed in the oxidation of the first anti-oxidant, are captured by the molecules of the second stabilizer, which reduces the probability of initiating oxidation. Thus, for example, the radicals of diphenyl nitrogen are captured by polyphenylene, which explains the increased hindrance of the oxidation of polypropylene by diphenylamine when polyphenylene is added.

Candidates in chemical sciences V. B. Miller and Yu. A. Shlyapnikov gave a paper on new developments in the mechanism of the action of anti-oxidants in the oxidation of polyolefins. The speakers noted that the only recently accepted theory of the action of inhibitors presupposes a linear consumption of inhibitor in the induction period, which gives a linear dependence of the induction period on the inhibitor concentration. Refinements of this theory by N. N. Semenov, who showed that a minimum "critical" concentration of inhibitor is required to slow up a branched chain reaction, have made it possible to explain the deviation of the relationship from linearity at low inhibitor concentrations, but have not succeeded in explaining the deviations at high concentrations, which are observed experimentally. In this work a study was made of the relation between the induction period for the oxidation of polypropylene near 200° and the inhibitor concentration, the temperature, and the oxygen pressure. The inhibitors used were aromatic amines and phenols. To explain the causes of the deviation of the experimental relationship from linearity, a study was made of the change in concentration of inhibitor in the induction period. For this purpose a method was worked out for extracting inhibitor from the partially oxidized polymer samples. It turned out that the inhibitor is consumed mainly on account of oxidation and in secondary processes connected with the oxidation of the inhibitor in which the polymer takes part, the oxidation of the later being thereby initiated. Apparently the inhibitor can also take part in the degenerate chain branching event, thereby changing the yield of free radicals in the hydroperoxide decomposition. In inhibiting the oxidation of polypropylene with paraphenylenediamine derivative it was shown that the original inhibitor is consumed practically completely long before the end of the induction period, after which the reaction is slowed up by various transformation products of the original inhibitor. In all cases the mechanism of oxidation in the presence of an inhibitor is very complicated.

Candidate in chemical sciences A. N. Pravednikov gave a report on the subject: "Mechanism of Radiation Structuration and Destruction of Polymers". The primary act in the interaction of radiation with a polymer, independently, of its chemical structure, was said by the speaker to be tearing off an electron to form a positive ion. Neutralization of this ion by an electron causes the formation of an excited molecule, which decomposes later to form free radicals. The nature of the changes going on in the structure of the polymer, will, obviously, depend on the stabilization mechanism of these radicals. In the radiolysis of polyolefines or other structurizing polymers, the hydrogen atom, formed by rupturing the C-H bond and having at first an increased energy ("hot" hydrogen atom), will tear off hydrogen from the neighboring polymer molecule, and the radical formed in this process will recombine with the first radical to form a cross linkage. The rate of this reaction will obviously be independent of the temperature. The hydrogen atoms, having "thrown away" their excess energy, will tear off hydrogen from polymer molecules located at large distances from the place where the first radical was formed. In this case, the only radicals that will be able to enter into the recombination reaction will be those which are not too far removed from one another, and the yield of the structuration reaction will depend on the temperature.

In any discussion of radical reactions in polymer systems it must be kept in mind that tearing a hydrogen atom out of a molecule is accompanied by a transition of that part of the molecule from the tetrahedral configuration to a plane. In the case of polymers this transition causes a rearrangement of the parts of the chain involved, which leads to increased activation energy in the reaction, and, consequently, to a reduction in the rate of the reaction. Carrying hydrogen atoms from the side groups of the polymer chains was said by the speaker not to cause any rearrangement of the parts of the chain, and, consequently, will have a lower activation energy. Therefore, putting side groups into

the chain will favor an increase in the reaction rate of the "cold" hydrogen atoms with polymer chains, located in the immediate vicinity of the place where the first radical is formed. The fact that so far no one has been able to observe structuration processes going on in the radiolysis of polymers containing quaternary carbon atoms (polyisobutylene, poly- $\alpha$ -methylstyrol), as well as the data on the nature of the temperature dependence of their rate of destruction, gives some reason for the speaker to think that in the case of these polymers, the radicals formed by tearing off side groups or hydrogen atoms, react with one another, because of steric hindrance, by rupturing the main chain of the polymer molecule.

The study of the radiolysis of copolymers of styrol and  $\alpha$ -methylstyrol in the swelled state has shown, that in this case, as a result of the absence of steric hindrance in the reaction of polymer radicals with radicals formed from the solvent, there is penetration of solvent molecules into the polymer chain (shown by the method of marked atoms), and the rate of destruction of the polymer is here lowered. The data obtained by the speaker from studying the radiolysis of a mixture of low molecular radioactive polyisobutylene with ordinary high molecular polyisobutylene show that the reaction with one another of the radicals formed in the radiolysis of this polymer represents a peculiar type of disproportionation reaction, accompanied by the transfer of a low molecular group from one polymer radical to the other. The formation of cross linkages in the radiolysis of polystyrol is accompanied by the transfer of a low molecular group from one polymer radical to the other. The formation of cross linkages in the radiolysis of polystyrol is accompanied by the expenditure of considerably more energy than is the case when using radiation to sew up the structure of polymers which do not contain phenyl groupings, as, for example, polyethylene. If 25-35 ev is used up in the formation of one cross linkage during the radiolysis of polyethylene, in the radiolysis of polystyrol this quantity grows to 3000-5000 ev. At the same time the yield of free radicals from irradiation of linear paraffins is only 5-7 time greater than the yield of radicals from alkylaromatic compounds. Thus, the high radiation stability of polystyrol cannot be explained by the usual scheme of the protective action of the benzene rings. Experiments made on model systems have shown that the high stability of polystyrol is concerned very largely with the occurrence of a disproportionation reaction between the initial radicals and the cyclohexadienyl radicals, formed by the union of a hydrogen atom to a benzene ring.

During the session a paper was also given by Academician I. V. Tananaev on the subject: "Status and Problems of Research in the Field of Inorganic Polymers".

The discussions after the papers were participated in by Doctor of Chemical Science M. G. Gonikberg, Corresponding Member of the Academy of Sciences, USSR V. V. Korshak, Doctors of Chemical Sciences A. A. Trapeznikov and V. L. Tal'roze, Corresponding Members of the Academy of Sciences, USSR, A. A. Korotkov and K. A. Kocheshkov, Academicians V. I. Speitsyn and S. I. Vol'skovich and others.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY  
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LEIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab. - Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. -Publisher.

# Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol. Issue Year
AE	Atomnaya energiya	Soviet Journal of Atomic Energy	Consultants Bureau	1 1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics - Acoustics	American Institute of Physics	1 1955
Astr.(on), zh.(urn).	Antibiotiki	Antibiotics	Consultants Bureau	4 1959
Avto(mat), sverka	Astronomicheskii zhurnal	Soviet Astronomy-AJ	American Institute of Physics	34 1957
	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)	1 1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27 1956
	Biofizika	Biophysics	National Institutes of Health*	1 1957
Byull. eksp(erim). biol. i med.	Biokhimiya	Biochemistry	Consultants Bureau	21 1956
DAN (SSSR)	Byulleten' eksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41 1959
Dokl(ad)y AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows: Doklady Biochemistry Section Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology, microbiology, morphology, parasitology, physiology, zoology sections) Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections) Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology Proceedings of the Academy of Sciences of the USSR, Section: Chemistry Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections) Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry Proceedings of the Academy of Sciences of the USSR, Sections: Geology Doklady Soviet Mathematics Soviet Physics-Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections) Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections) Wood Processing Industry Telecommunications Entomological Review Pharmacology and Toxicology Physics of Metals and Metallurgy Schenov Physiological Journal USSR Plant Physiology Geochemistry Soviet Physics-Solid State Measurement Techniques Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences	American Institute of Biological Sciences American Institute of Biological Sciences	106 1956 112 1957
		Life Sciences	American Institute of Biological Sciences	112 1957
		Chemical Sciences	Consultants Bureau	106 1956
			Consultants Bureau	106 1956
			Consultants Bureau	112 1957
		Earth Sciences	American Geological Institute	124 1959
			Consultants Bureau	106- 1957- 123 6 1958
			Consultants Bureau	106- 1957- 123 6 1958
		Mathematics	The American Mathematics Society	131 1961
		Physics	American Institute of Physics	106 1956
			Consultants Bureau	106- 1956- 117 1957
			Timber Development Association (London)	9 1959
			Massachusetts Institute of Technology*	1 1957
			American Institute of Biological Sciences	38 1958
			Consultants Bureau	20 1957
			Acta Metallurgica*	5 1957
			National Institutes of Health*	1 1957
			American Institute of Biological Sciences	4 1957
			The Geochemical Society	1 1958
			American Institute of Physics	1 1959
			Instrument Society of America	1 1959
			Consultants Bureau	1 1952
Derevoobrabat. prom-st'.	Derevoobrabatvayushchaya promyshlennost'	Wood Processing Industry	American Institute of Physics	106 1956
	Elektrosvyaz	Telecommunications	Consultants Bureau	106- 1956- 117 1957
Entom(ol), oboz(renie)	Entomologicheskoe obozrenie	Entomological Review	Timber Development Association (London)	9 1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Massachusetts Institute of Technology*	1 1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallurgy	American Institute of Biological Sciences	38 1958
Fiziol. zhurn. SSSR	Fiziologicheskii zhurnal im. I. M. Sechenova	Schenov Physiological Journal USSR	Consultants Bureau	20 1957
(im. Sechenova) rast.	Fiziologiya rastenii	Plant Physiology	Acta Metallurgica*	5 1957
Fiziol(ogiya) rast.	Geokhimiya	Geochemistry	National Institutes of Health*	1 1957
FTT	Fizika tverdogo tela	Soviet Physics-Solid State	American Institute of Biological Sciences	4 1957
Izmerit. tekhnika	Izmeritel'naya tekhnika	Measurement Techniques	The Geochemical Society	1 1958
Izv. AN SSSR	Izvestiya Akademii Nauk SSSR	Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences	American Institute of Physics	1 1959
O(td), Kh(im), N(auk)	Otdelenie khimicheskikh nauk		Instrument Society of America	1 1959
			Consultants Bureau	1 1952



continued

Izv. AN SSSR, Otdel. Tekhn. N(auk): Met(ali). I top.	(see Met. I top.)	Bulletin of the Academy of Sciences of the USSR; Physical Series	1	1954
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	American Geological Institute	1	1958
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Research Association of British Rubber Manufacturers	18	1959
Kauchuk i rezina	Kauchuk i rezina	Consultants Bureau	1	1960
	Kinetika i kataliz	Coal Tar Research Association	1	1958
	Koks i khimiya	Consultants Bureau (Leeds, England)	1	1952
	Kolloidnyi zhurnal	American Institute of Physics	2	1957
Kolloidn. zh(urn).	Kristallografiya	Acta Metallurgica	6	1958
	Metallovedenie i termicheskaya obrabotka metallov	Acta Metallurgica	1	1957
	Metallurg	Eagle Technical Publications	1	1960
	Metallurgiya i topliva	American Institute of Biological Sciences	26	1957
	Mikrobiologiya	American Institute of Physics	6	1959
	Optika i spektroskopiya	American Institute of Biological Sciences	1	1958
	Pochvovedenie	British Scientific Instrument Research Association	1	1959
	Priborostroenie	Instrument Society of America	1	1957
Priboiy i tekhn. eksperimenta	Priboiy i tekhnika eksperimenta	Instrument Society of America	1	1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	American Society of Mechanical Engineers	1	1958
PTÉ	(see Priboiy i tekhn. éks.)			
Radiotekh. i elektronika	Problemy Severa	National Research Council of Canada	1	1957
	Radiotekhnika	Massachusetts Institute of Technology*	12	1957
	Stanki i instrument	Massachusetts Institute of Technology*	2	1957
	Sterilizatsiya	Production Engineering Research Assoc.	1	1959
	Steklo i keramika	Iron and Steel Institute	1	1959
	Svarochnoe proizvodstvo	Consultants Bureau	13	1956
	Teoriya veroyatnostei i ee primeneniye	British Welding Research Association	4	1959
	Tsvetnyye metally	Society for Industrial and Applied Mathematics	1	1956
Tsvet. Metally	Uspekhi fizicheskikh Nauk	Primary Sources	1	1960
UFN	Uspekhi khimii	American Institute of Physics	66	1958
UMN	Uspekhi matematicheskikh nauk	The Chemical Society (London)	1	1960
Usp. khim(ii)	(see UFN)	London Mathematical Society	15	1960
Usp. fiz. nauk	(see UFN)			
Usp. matem. nauk	(see UFN)			
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Oliver and Boyd	48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Production Engineering Research Assoc.	4	1959
Vop. gem. i per. krov	Voprosy gematologii i perelivaniya krov	National Institutes of Health*	1	1957
Vop. onk.	Voprosy onkologii	National Institutes of Health*	1	1957
Vop. virusol.	Voprosy virusologii	National Institutes of Health*	1	1957
Zav(odsk), lab(oratoriya)	Zavodskaya laboratoriya	Consultants Bureau	25	1952
Zh(urn) Zh. anal(it), khim(ii)	Zhurnal analiticheskoi khimii	American Institute of Physics	28	1955
ZhETF	Zhurnal eksperimental'noi i teoreticheskoi fiziki	The Chemical Society (London)	7	1959
Zh. éksp(erim.) i teor. fiz.	Zhurnal fizicheskoi khimii	National Institutes of Health*	1	1957
ZhFZh Zh. fiz. khim(ii)	Zhurnal fizicheskoi khimii	The Chemical Society (London)	1	1959
ZhMEI Zh(urn), mikrobiol., épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	National Institutes of Health*	1	1957
ZhNKh	Zhurnal neorganicheskoi khimii	The Chemical Society (London)	1	1959
Zh(urn), neorgan(ich), khim(ii)	Zhurnal obshchei khimii	Consultants Bureau	19	1949
ZhOKh	Zhurnal obshchei khimii	Consultants Bureau	23	1950
ZhPKh	Zhurnal prikladnoi khimii	Consultants Bureau	1	1960
Zh(urn), prikl. khim(ii)	Zhurnal strukturnoi khimii	American Institute of Physics	25	1956
ZhSKh	Zhurnal strukturnoi khimii	National Institutes of Health*	1	1958
Zh(urn), strukt. khim(ii)	Zhurnal tekhnicheskoi fiziki			
ZhTF	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)			
Zh(urn), tekhn. fiz.				
Zh(urn), vyssh. nervn. deyat. (im. Pavlova)				

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